Aromatic Heterocycles Containing Arsenic and Sulfur: The Synthesis of 1,2- and 1,3-Thiaarsole and the Gas-Phase Molecular Structure of 1,2-Thiaarsole

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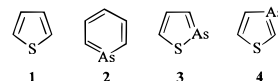
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Abstract: The reaction of chloromethyl ethynyl sulfide with Bu_2SnH_2/LDA affords 2,3-dibutyl-2,3-dihydro-1,3-thiastannole which on reaction with $AsBr_3$ followed by DBU affords 1,3-thiaarsole in 22% yield. The reaction of allyl mercaptan with 2 equiv of BuLi followed by 1 equiv of Me_2SnCl_2 affords an 80% yield of 2,3-dihydro-2,2-dimethyl-1,2-thiastannole which on reaction with $AsBr_3$ followed by DBU gives 1,2-thiaarsole in 56% yield. The NMR, UV and mass spectra are consistent with aromaticity of both thiaarsoles. The structure of 1,2-thiaarsole, measured by electron diffraction, suggests that it is an aromatic compound. The thermal average bond lengths (r_g/Å) and bond angles ($\angle_\alpha$/deg) with estimated 2σ uncertainties are $r(\text{C}-\text{H}) = 1.078(14)$, $r(\text{C}_3-\text{C}_4) = 1.414(10)$, $r(\text{C}_4-\text{C}_5) = 1.382(9)$, $r(\text{As}-\text{C}) = 1.829(4)$, $r(\text{S}-\text{C}) = 1.711(5)$, $\angle(\text{CCC}) = 118.0(12)$, $\angle(\text{AsCC}) = 117.7(10)$, $\angle(\text{SCC}) = 117.9(9)$, $\angle(\text{SAsC}) = 89.8(5)$, $\angle(\text{AsSC}) = 96.6(4)$. Ab initio molecular orbital calculations at the B3LYP/6-31G* level were performed for both thiaarsoles.

Introduction

Simple fully unsaturated heterocycles are of substantial intrinsic interest. The discovery of thiophene (**1**) by Victor Meyer in 1883 was central to the development of the concept of aromaticity.[1−3] More recent investigations of arsabenzene (**2**)[4−7] and related arsenic−nitrogen heterocycles[8−10] have been important for the study of multiple bonding between carbon and the heavier main group elements. The arsenic−sulfur

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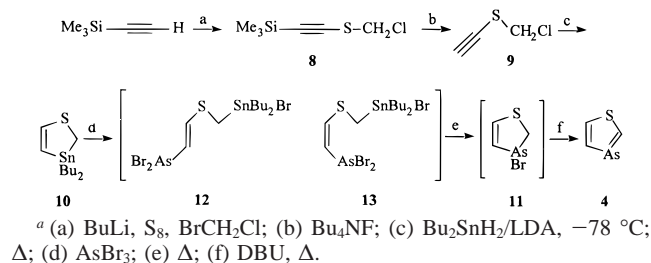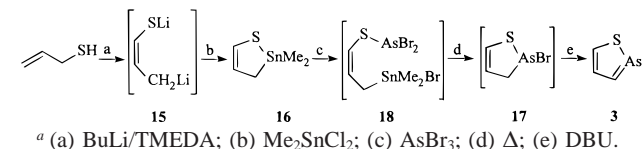

containing heterocycles 1,2-thiaarsole (**3**) and 1,3-thiaarsole (**4**) might be expected to resemble **1** and **2**. We report here on the details of the synthesis of **4** which was published earlier.[11] We also report an efficient synthesis of the new heterocycle **3**. The availability of **3** in gram quantities has allowed us to make an electron-diffraction determination of its structure which suggests that 1,2-thiaarsole is a genuinely aromatic compound.

Syntheses

The original synthesis of arsabenzene, as outlined in Scheme 1, involves the reaction of 1,4-pentadiyne (**5**) with dibutylstannane to produce 1,1-dibutylstannacyclohexa-2,5-diene (**6**).[12]

Scheme 1[a]
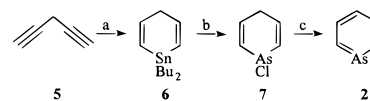
[a] (a) Bu_2SnH_2; (b) $AsCl_3$; (c) Δ or DBU.

On treatment with $AsCl_3$ **6** undergoes facile As/Sn exchange to give 1-chloroarsacyclohexadiene (**7**) which loses HCl on heating or on treatment with base to afford arsabenzene.[7] Since our syntheses of thiaarsoles **3** and **4** are analogous, we initially sought to prepare the corresponding tin heterocycles **10** and **16**, respectively (see Schemes 2 and 3).

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Scheme 2[a]

[a] (a) BuLi, S_8, BrCH$_2$Cl; (b) Bu$_4$NF; (c) Bu$_2$SnH$_2$/LDA, −78 °C; Δ; (d) AsBr$_3$; (e) Δ; (f) DBU, Δ.

Scheme 3[a]

[a] (a) BuLi/TMEDA; (b) Me$_2$SnCl$_2$; (c) AsBr$_3$; (d) Δ; (e) DBU.

The synthesis of **10**[13] starts from commercially available (trimethylsilyl)acetylene, which following a procedure of Brandsma,[14] is lithiated and reacted sequentially with sulfur followed by bromochloromethane to afford chloromethyl trimethylsilylethynyl sulfide (**8**) in 60% yield. Desilylation of **8** with Bu$_4$NF in methanol gives the labile chloromethyl ethynyl sulfide (**9**) in 70% yield. Using an adaption of a ring-closure procedure pioneered by Jousseaume and co-workers,[15] **9** is treated with LiSnHBu$_2$ at −78 °C followed by gentle warming and distillation to afford a 39% yield of the desired tin heterocycle **10**. Apparently this reaction takes place via nucleophilic displacement of the chloride by the tin anion followed by intramolecular hydrostannation of the ethynyl group on heating.

The reaction of AsBr$_3$ with **10** is complex but can be monitored by ^{1}H NMR spectroscopy. In CDCl$_3$ at 25 °C excess AsBr$_3$ and **10** quickly give a 3:1 mixture of **12**/**13**. On heating to 80 °C for 7 h a fine precipitate forms while the ^{1}H NMR spectrum of the CDCl$_3$ solution shows a 3:1 mixture of Bu$_2$-SnBr$_2$ and **11**. Apparently this conversion is limited by the prior E/Z-isomerization of **13** to **12** which cannot form the ring-closed **11**. Preparatively it is most convenient to simply heat a mixture of **10** and AsBr$_3$ in tetraglyme followed by treatment with DBU. This allows distillation of **4** in 22% yield. 1,3-Thiaarsole is an air-sensitive liquid which is most conveniently handled in dilute solution.

The synthesis of **16** is based on Seebach's observation that commercially available allyl mercaptan can be easily dilithiated to **15** with BuLi in THF/TMEDA.[16] Reaction of **15** with dimethyltin dichloride affords the crystalline 2,3-dihydro-2,2-dimethyl-1,2-thiastannole (**16**) in 79% isolated yield. The reaction of **16** with AsBr$_3$ in CDCl$_3$ can also be monitored using ^{1}H NMR spectroscopy. **16** is quickly converted to **17** apparently via the intermediacy of **18**. Again, it is most convenient to heat **16** with AsBr$_3$ in tetraglyme followed by treatment with DBU. 1,2-Thiaarsole can be isolated directly by distillation in 56% yield. The pale yellow liquid **3** is quite air-sensitive. On standing at room temperature as a neat liquid for several days, it slowly forms a white, apparently polymeric precipitate.

Table 1. NMR Chemical Shifts Compared: ^{1}H and ^{13}C NMR (Brackets) for Thiophene (**1**), Arsabenzene (**2**), 1,2-Thiaarsole (**3**), and 1,3-Thiaarsole (**4**)[a,b]

chemical shift	compound			
	1	**2**[c]	**3**	**4**[d]
H(2)[C(2)]	7.35[124.2]	9.68[167.7]		9.91[167.9]
H(3)[C(3)]	7.13[126.2]	7.83[133.2]	10.02[e][177.7]	
H(4)[C(4)]		7.51[128.2]	8.15[e][143.3]	8.94[155.7]
H(5)[C(5)]			8.54[e][138.5]	8.48[139.5]

[a] Solvent, CDCl$_3$. [b] ^{1}H NMR (400 MHz) and ^{13}C NMR (126 MHz). [c] ref 11. [d] ref 8. [e] $J_{H(3)H(4)}$, 6.0 Hz; $J_{H(3)H(5)}$, 0.6 Hz; $J_{H(4)H(5)}$, 5.0 Hz.

In summary, 1,2-thiaarsole and its 1,3-isomer are available via short syntheses from commercially available starting materials. Unfortunately the four-step synthesis of **4** has an overall yield of only 3%. Since the 1,2-thiaarsole is available in two easy steps in an overall yield of 45%, it is far easier to obtain in multigram quantities.

Spectra

The first order ^{1}H NMR spectra of **3** and **4**, summarized in Table 1, are readily assigned since the chemical shift values of the protons adjacent to arsenic occur at particularly low field. Similar low field signals are shown by the α-protons of arsabenzene[7,17] and various arsenic−nitrogen[8-10] heterocycles. In the case of arsabenzene it has been proposed that this deshielding is due to a magnetic anisotropy of π-electrons centered on arsenic.[17] The McConnell equation indicates that protons in the ring plane experience maximum deshielding which drops off inversely with cube of the distance from arsenic.[18] Application of this treatment to **3** and **4** indicates that protons adjacent to arsenic should be strongly deshielded as observed. Although the more remote protons of **3** and **4** should be less strongly effected by the arsenic anisotropy, all protons should experience an anisotropic effect due to the aromatic ring current of the heterocycles. Thus, the fact that all of the proton signals of **3** and **4** are downfield from those of thiophene argues for a substantial ring current[19] and hence to aromaticity of the thiaarsoles.

The ^{13}C NMR spectra of **3** and **4** (Table 1) are easily assigned by examining the cross-coupling with the proton signals. The chemical shift values for carbon atoms α to arsenic occur in the range δ 156−178. Generally carbon π-bonding to arsenic results in substantial deshielding relative to compounds with C−C π-bonds. Thus, nonaromatic compounds with full C−As double bonds show signals in the range δ 212−185.[20] The partial C−As π-bonding of the C(2) of arsabenzene results in a signal at δ 168.[17] The similar range of signals for the α carbon atoms of **3** and **4** is consistent with that for similar delocalized As−C π-bonding.

Thiophene,[21] arsabenzene,[7] 1,2-thiaarsole, and 1,3-thiaarsole show mass spectra (EI, 70 eV) which are typical of aromatic compounds. In all cases the molecular ion is the base peak, and loss of acetylene m/e, (M$^+$ − 26) is a major fragmentation pathway. The (CHS$^+$) ion is an important daughter ion for **4** as it is for **1**. On the other hand, **3** shows the largest daughter ion at m/e, 107 for loss of [C$_3$H$_3$], while loss of [As] at m/e, 71 is also important. This difference requires that the isomers **3** and **4** maintain their identity during fragmentation.

Finally the UV spectrum of **3** shows peaks at 307 (4300), 272 (2600), and 222 (2700) nm, which are rather close to the

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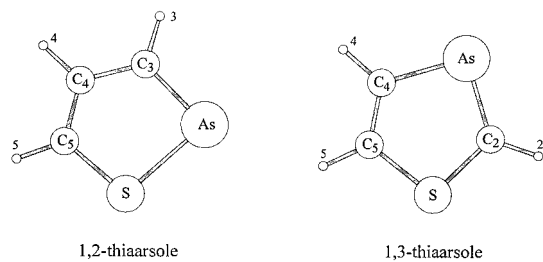
Figure 1. Diagrams of 1,2-thiaarsole and 1,3-thiaarsole.

Table 2. Bond Distances (r/Å) and Bond Angles ($\angle$/deg) in 1,2-Thiaarsole and 1,3-Thiaarsole[a]

	1,2-thiaarsole			1,3-thiaarsole	
	experiment[b]	theory[c]			theory[c]
parameter	r_g/Å	r_e/Å;$\angle_\alpha$/deg	parameter		r_e/Å;$\angle_\alpha$/deg
$\langle r(\text{C}-\text{H})\rangle$	1.078 (14)	1.086	$\langle r(\text{C}-\text{H})\rangle$		1.085
$r(\text{C}_4-\text{C}_5)$	1.382(9)	1.357	$r(\text{C}_4-\text{C}_5)$		1.360
$r(\text{C}_3-\text{C}_4)$	1.414(10)	1.410	$r(\text{S}-\text{C}_2)$		1.714
$r(\text{S}-\text{C})$	1.711(5)	1.724	$r(\text{S}-\text{C}_5)$		1.731
$r(\text{As}-\text{C})$	1.829(4)	1.826	$r(\text{As}-\text{C}_2)$		1.821
$r(\text{As}-\text{S})$	2.198(3)	2.245	$r(\text{As}-\text{C}_4)$		1.888
$\angle(\text{CCC})$	118.0(12)	118.1	$\angle(\text{SCAs})$		117.9
$\angle(\text{AsCC})$	117.7 (10)	118.9	$\angle(\text{CAsC})$		90.1
$\angle(\text{SCC})$	117.9(9)	118.2	$\angle(\text{AsCC})$		117.1
$\angle(\text{AsSC})$	96.6(4)	95.8	$\angle(\text{CCS})$		117.7
$\angle(\text{SAsC})$	89.8(5)	89.0	$\angle(\text{CSC})$		97.1
$\angle(\text{C}_4\text{C}_3\text{H}_3)$	123.8(61)	120.6	$\angle(\text{SC}_2\text{H}_2)$		116.3
$\angle(\text{C}_3\text{C}_4\text{H}_4)$	121.7(82)	121.6	$\angle(\text{AsC}_4\text{H}_4)$		122.4
$\angle(\text{C}_4\text{C}_5\text{H}_5)$	123.4(92)	124.5	$\angle(\text{C}_4\text{C}_5\text{H}_{56})$		126.1
	R^d	0.10			

[a] Atom numbering from Figure 1. [b] Values in parentheses are estimated 2σ. [c] B3LYP/6-31G*. [d] Goodness-of-fit factor: $R = [\Sigma_i w_i \Delta_i^2 / \Sigma_i s_i I_i(\text{obsd})^2]^{1/2}$ where $\Delta_i = s_i I_i(\text{obsd}) - s_i I_i(\text{calcd})$.

absorption maxima shown by **4** at 290, 267, and 225 nm. These bands are substantially red-shifted from those of thiophene at 215 and 231 nm. This shift to lower energy for the $\pi \rightarrow \pi^*$ excitations is an expected consequence of replacement of carbon by the larger arsenic.[8a,9a,10a,22] In summary, the various spectra of **3** and **4** are consistent with the designation of both thiaarsoles as aromatic compounds.

Theoretical Calculations

The structures of **3** and **4** were optimized ab initio with use of the program G98W[23] at the HF and B3LYP levels with the basis 6-31G*. The results are listed in Table 2 and the corresponding models diagrammed in Figure 1. The Cartesian force fields for **3** were used in the program ASYM40[24] to provide data about unobservable quantities that would be useful in the experimental structure investigation planned for this molecule.

Electron Diffraction of 1,2-Thiaarsole

The structure of **3** was measured by electron diffraction from the vapor at a nominal temperature of 24 °C. The refinements were carried out by least-squares,[25] fitting theoretical intensity curves to the experimental average curves. The methodology was as follows. The structure was defined in r_α space (the space representing the average *positions* of the atoms) by the parameters $r(\text{C}-\text{H})$, $\langle r(\text{C}-\text{C})\rangle = \frac{1}{2}[r(\text{C}_3-\text{C}_4) + r(\text{C}_4-\text{C}_5)]$, $\Delta r(\text{C}-\text{C}) = r(\text{C}_3-\text{C}_4) - r(\text{C}_4-\text{C}_5)$, $r(\text{As}-\text{C})$, $r(\text{S}-\text{C})$, $\angle(\text{C}-\text{C}-\text{C})$, $\angle(\text{As}-\text{C}-\text{C})$, $\angle(\text{S}-\text{C}-\text{C})$, $\angle(\text{C}_4-\text{C}_3-\text{H})$, $\angle(\text{C}_3-\text{C}_4-\text{H})$, and $\angle(\text{C}_4-\text{C}_5-\text{H})$; C_s symmetry for the molecule was assumed. To obtain the thermal average distances
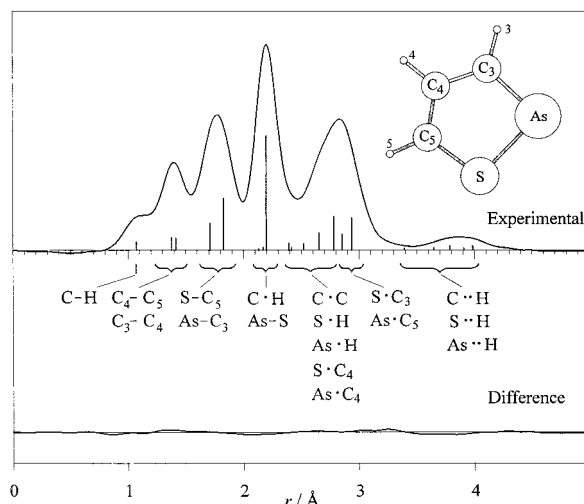
Figure 2. Radial distribution curves for 1,2-thiaarsole. The positions of the vertical bars denote interatomic distances and the bar lengths indicate the weight of the terms. The difference curve is experimental minus theoretical.

r_g, the distance corrections $r_g - r_\alpha$ obtained from the normal coordinate calculations were applied. It was necessary to use the method of predicates[26] for the difference $\Delta r(\text{C}-\text{C})$ and the hydrogen-angle parameters which could not otherwise be refined. The results for the principle distances and angles are found in Table 2; more details are found in the Supporting Information. The radial distribution of distances is shown in Figure 2.

Discussion

Although true r_e distances are not identical with r_g, for bonds in reasonably stiff molecules they are customarily only a few thousandths of an angstrom smaller. The r_e distances calculated ab initio are dependent on level of theory and basis set, but their accuracy from our calculation is expected to be good. As Tables 2 and S1 show, the agreement between experiment and theory for **3** is excellent.

Structure is an important aspect of aromatic character.[19b] In particular the lack of appreciable C—C bond alternation and

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the multiple bond character of the ring bonds of heterocycles such as arsabenzene are associated with their aromaticity. In this respect the heavy atom structure of 1,2-thiaarsole (**3**) is relevant since the ring bond lengths are shorter than "normal" covalent single bonds. The two carbon–carbon bond lengths have similar values. They differ by only 0.033(17) Å and average to 1.398 Å, essentially the same as the carbon–carbon distance in benzene and arsabenzene.[27] The As–C bond of **3** (1.829(4) Å) is 0.07–0.09 Å shorter than the nominal single bonds to the aliphatic heterocycles 2-methyl-1,3,2-dithiaarsolane (**19a**)[28] and 2-bromo-1,3,2-dithiaarsolane (**19b**).[29] The As–C bond is also about 0.027 Å shorter than that of arsabenzene, but in the same range as those of various aromatic arsenic–nitrogen heterocycles.[8–10] On the other hand, this bond is a bit longer than that in compound **20** which has a congested As–C double bond[20b] (As–C, 1.794(11) Å). Clearly the As–C bond of **3** is intermediate in length between a single and double bond. The C–S bond of **3** is about 0.10 Å shorter than those of **19a,b** (1.805(9) Å), but its length is very close to the value of that in the thiophene (1.714(1) Å,[30a] 1.717(4) Å[30b]) where this bond is clearly "aromatic".
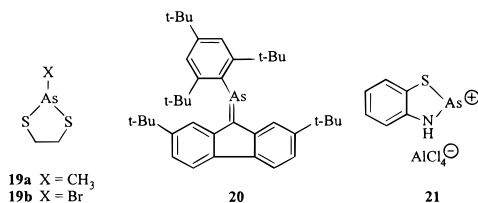
It is more difficult to draw conclusions about the As–S bond (2.198(3) Å) in **3** from similar comparisons. The bond is slightly shorter (0.02–0.05 Å) than the nominal As–S single bonds of thiaarsolanes,[28,29] but there are few compounds which have As–S bonds with double-bond character. We note that Burford and co-workers have reported on the structure of the 1,3,2-benzo-thiazolium AlCl₄ salt (**21**), which appears to have As–S pπ-pπ bonding.[31] Although the As–S bond of **21** (2.154(4) Å) is 0.04 Å shorter than that of **3**, the difference in charge type makes detailed comparison tenuous.

The bond angles of **3** at the carbon atoms are also consistent with aromaticity. They average 117.9° and differ by no more than 0.3°, which implies similar bond hybridizations, and is a likely consequence of the similar bond orders of the links on either side of each carbon atom. The bond angle at arsenic is smaller than at sulfur. Both angles are several degrees smaller than those of acyclic molecules which can be understood as the result of constraints imposed by the aromatic carbon atoms of the ring coupled with the long sulfur–arsenic bond. In summary the structure of 1,2-thiaarsole is consistent with it being a genuinely aromatic ring.

Since the agreement between the experimental and theoretical structures for the 1,2-thiaarsole are excellent, it is likely that
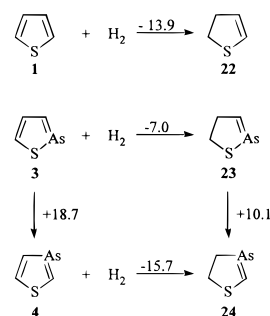

Figure 3. Enthalpies of hydrogenation (kcal/mol) of the thiaarsoles and related molecules.

the calculated structure for the 1,3-thiaarsole is similarly accurate. Comparison of the theoretical structures of **3** and **4** shows several noteworthy differences. First, the C–C bond of **4** (1.360 Å) is a slightly shorter than those of **3**, but still a bit above the range characteristic of normal C–C double bonds. Second, the C₂–As bond of **4** has a length (1.789 Å) close to the C–As double bond of **20**, while the As–C₄ bond (1.883 Å) approaches the length of an As–C single bond.[28,29] The C–S bonds of **4**, with lengths of 1.721 and 1.703 Å, are in the range shown by thiophene and substituted thiophenes.[30] Overall, the structure of 1,3-thiaarsole suggests a molecule with more localized alternating single and double bonds.

The more localized bonds of **4** relative to **3** imply that the aromatic stabilization energy of **4** should be lower than for **3**. Aromatic stabilization energies have often been derived from enthalpy of hydrogenation data,[32] and thus it is reasonable to expect that the differences between the enthalpies of hydrogenation are a crude measure of the differences in the aromatic stabilization energies of our heterocycles.[33] We have calculated (B3LYP/6-31G*) the total energies at 298 K of the optimized structures of **1**, **3**, and **4** and their (non-aromatic) dihydro derivatives **22**, **23**, and **24**. From these we obtained the enthalpies of monohydrogenation of **1**, **3**, and **4**; the results are summarized in Figure 3. It is seen that the enthalpy of the thiophene reaction **1** → **22** (−13.86 kcal/mol) is similar to that of the 1,3-thiaarsole reaction **4** → **24** (−15.71 kcal/mol), which implies that these two molecules have similar aromatic stabilization energies. However, the enthalpy of hydrogenation of 1,2-thiaarsole **3** → **23** (−7.04 kcal/mol) is 8.67 kcal/mol less than that of the 1,3 compound, which suggests that the aromatic stabilization energy of **3** is about 9 kcal/mol greater than that of **4**. One also notes from Figure 3 that, taking the enthalpies as a measure of stability, **3** is 18.7 kcal/mol more stable than **4**. On the other hand, **23** is only about 10.1 kcal/mol more stable than **24**. Thus the greater delocalization energy of **3** is responsible for about half the energy difference between **3** and **4**. The remainder of the difference must be due to the number and type of bonds in the frame of each molecule. For example, **3** has one more each of C–C and As–S bonds than **4**, while **4** has one more each of As–C and S–C bonds.

Conclusions

We have prepared the new heterocycles 1,2-thiaarsole and 1,3-thiaarsole. The ¹H NMR, ¹³C NMR, UV, and mass spectra

19a X = CH₃
19b X = Br

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are consistent with the aromaticity of both thiaarsoles. The gas-phase structure of 1,2-thiaarsole was measured by electron diffraction. The C−C, C−As, and C−S bond lengths are intermediate between those of single and double bonds which is as expected for an aromatic structure. Ab initio MO calculations were performed on both thiaarsoles, thiophene, and their dihydroderivatives. Comparison of the calculated energies indicates that the aromatic delocalization energy of 1,2-thiaarsole is greater than those of 1,3-thiaarsole and thiophene.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of nitrogen or argon. Solvents were dried using standard procedures. The mass spectra were determined using either a VG-70-S spectrometer or a tandem Hewlett-Packard 5890 gas chromatograph/Finnigan 4023 quadruple mass spectrometer. The NMR spectra were obtained using Bruker AC-200, Bruker AM 300, Varian Inova-300, or Varian Inova-400 spectrometers. The ^{1}H NMR and ^{13}C NMR spectra were calibrated by using signals from solvents referenced to Me_4Si. The UV spectra were recorded on a Shimadzu UV 160U spectrometer. The combustion analyses were performed by Analytical Services Department of the Department of Chemistry (University of Michigan) using a Perkin-Elmer 240 CHN analyzer. 3,3-Dibutyl-2,3-dihydro-1,3-thiastannole was prepared by a literature procedure.[13] All other compounds are commercially available.

3-Bromo-2,3-dihydro-1,3-thiaarsole (11). Excess AsBr$_3$ was added to a colorless solution of **10** in CDCl$_3$ in a 5 mm NMR tube at 25 °C. The solution immediately turned yellow. The ^{1}H NMR spectrum was recorded and was consistent with a mixture of **13**:**12**:**11** in the ratio 22:72:6. **13**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.63 (s, $^2J_{SnH}$ = 35.4 Hz, 2H); 7.00 (d, *J* = 9.0 Hz, 1H); 7.35 (d, *J* = 9.0 Hz, 1H). **12**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.57 (s, $^2J_{Sn-H}$ = 36.4 Hz, 2H); 6.89 (d, *J* = 9.0 Hz, 1H); 7.31 (d, *J* = 9.0 Hz, 1H). The reaction mixture was heated to 80 °C for 7 h. A fine precipitate formed. ^{1}H NMR spectroscopy of the solution showed only peaks for **11** and Bu$_2$SnBr$_2$ in the ratio of 1:3. Products were not isolated. **11**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.63 (s, 2H); 7.06 (d, *J* = 7.3 Hz, 1H); 7.76 (d, *J* = 7.3 Hz, 1H). ^{13}C NMR (90 MHz, CDCl$_3$) δ 34.5, 127.0, 152.0. MS (EI): (*m/e*, intensity) 228 (M$^+$, for C$_3$H$_4$As^{81}BrS).

1,3-Thiaarsole (4). A solution of AsBr$_3$ (1.0 g, 3.27 mmol) in 2 mL of tetraglyme was added to 4 mL of solution of **10** (1.03 g, 3.27 mmol) at −30 °C. A red suspension formed immediately. The mixture was heated to 85 °C for 15 h. Analysis by GC/MS indicated the coexistence of **11** and **4**. Excess DBU (1.0 mL, 6.7 mmol) was added, and the reaction mixture was allowed to stand at 85 °C for 3 h. On cooling to 25 °C the product (0.10 g, 22%) was distilled as a yellow liquid. MS(EI): *m/e* (intensity): 146 (100), 120 (51), 75 (13), 45 (19). UV (hexane): nm 225 (14,000), 267 (6200), 290 (9800).

2,3-Dihydro-2,2-dimethyl-1,2-thiastannole (16). A solution of butyllithium in hexane (18.2 mL, 45.6 mmol) was added dropwise to a solution of allyl mercaptan (1.61 g, 21.7 mmol) and TMEDA (3.30 mL, 21.7 mmol) in 40 mL of THF at 0 °C. The reaction mixture was stirred 4 h at 0 °C and then was cooled to −78 °C. A THF solution of

dimethyltin dichloride (5.26 g, 23.4 mmol) was added to the reaction mixture dropwise via cannula. After the addition was complete, the mixture was allowed to warm to room temperature and stir overnight. Volatiles were removed in vacuo, and the residue was extracted twice with pentane. The combined extracts were filtered, and the solvent was removed in vacuo. The resulting solid was washed twice with ice cold pentane and dried under reduced pressure to afford **16** as a light yellow solid. Yield: 79% (3.6 g); mp (uncorr) 97 °C. ^{1}H NMR (CDCl$_3$) δ 6.28 (dt, *J* = 7.7, 2.0 Hz, 1H); 6.22 (dt, *J* = 7.7, 3.6 Hz, 1H); 2.01 (dd, *J* = 3.5, 2.1 Hz, 2H); 0.63 (s, 6H). ^{13}C NMR (CDCl$_3$) δ 126.0, 125.9, 19.0, 3.6. HRMS (CI, NH$_3$) calcd for M + H) C$_5$H$_{11}$S^{120}Sn: 222.9603; Found: 222.9612. MS (CI, NH$_3$): 223 (100), 207 (4), 120 (36). Analytically pure sample was obtained by vacuum sublimation. Anal. Calcd for C$_5$H$_{10}$SSn: C, 27.14; H, 4.40. Found: C, 27.14; H, 4.40.

2-Bromo-2,3-dihydro-1,2-thiaarsole (17). A solution of **16** (0.74 g, 3.35 mmol) in 15 mL of methylene chloride was added dropwise to a solution of AsBr$_3$ (1.11 g, 3.35 mmol) in 10 mL of methylene chloride. Volatiles were removed in vacuo leaving a 1:1 mixture of Me$_2$SnBr$_2$ and **17** as a waxy mixture which was difficult to separate. Total weight of the mixture was 1.78 g, NMR yield of **17** estimated to be 98%. ^{1}H NMR (CDCl$_3$) δ 6.52 (dt, *J* = 6.1, 2.1 Hz, 1H); 6.43 (dt, *J* = 6.1, 3.2 Hz, 1H); 3.75 (dd, *J* = 3.2, 2.1 Hz, 2H). ^{13}C NMR (CDCl$_3$) δ 126.9, 126.8, 50.1. MS(EI, *m/e* (intensity): 228 (25, M$^+$ calcd for C$_3$H$_4$As^{81}BrS), 147 (100). HRMS(EI) calcd for C$_3$H$_4$As^{79}BrS: 225.8433. Found 225.8437.

1,2-Thiaarsole (3). A solution of AsBr$_3$ (4.37 g, 13.9 mmol) in 40 mL of tetraglyme was added dropwise to a suspension of **16** (3.05 g, 13.8 mmol) in 30 mL of tetraglyme at 25 °C. The reaction mixture was then heated to 50−60 °C and stirred overnight. The solution was cooled to 0 °C, and DBU (2.0 mL, 13.4 mmol) was added dropwise by syringe, causing a precipitate to form. After the addition the reaction mixture was allowed to warm to room temperature and stir for 3 h. The mixture was distilled, giving **3** as a yellow liquid (bp 65 °C at 0.03 Torr). Yield: 56% (1.32 g). UV (hexanes) nm (E): 222 (2700), 272 (2600), 307 (4300). HRMS (EI) calcd for C$_3$H$_3$SAs: 146.9171; Found: 146.9178. MS (EI) Me (intensity): 146 (100), 120 (9), 107 (36), 71 (11). Anal. Calcd for C$_3$H$_3$SAs: C, 24.67; H, 2.07. Found: C, 24.12; H, 2.06.

Supporting Information Available: Table S1 of all important interatomic distances (r_α, r_g, and r_a) and amplitudes of vibration. Table S2 correlation matrix for refined parameters. Table S3 of the scattered intensities from electron diffraction. Figure S1 of intensity curves (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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