

Structural characteristics of 2-halo-1,3,2-dithiarsenic compounds and tris-(pentafluorophenylthio)-arsen

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Abstract

The combination of various dithiols and AsX_3 ($\text{X} = \text{F}, \text{Cl}$) produces the series of cyclized halo-arsenic dithiolate compounds: 2-chloro-1,3,2-dithiarsolane [$\text{AsCl}(\text{SCH}_2\text{CH}_2\text{S})$] (**1**), 2-iodo-1,3,2-dithiarsolane [$\text{AsI}(\text{SCH}_2\text{CH}_2\text{S})$] (**2**), 2-chloro-1,3,2-dithiarsenane [$\text{AsCl}(\text{SCH}_2\text{CH}_2\text{CH}_2\text{S})$] (**3**), 2-iodo-1,3,2-dithiarsenane [$\text{AsI}(\text{SCH}_2\text{CH}_2\text{CH}_2\text{S})$] (**4**), 3-chloro-4H,7H-5,6-benz-1,3,2-dithiarsepine [$\text{AsCl}(\text{SCH}_2)_2(\text{C}_6\text{H}_4)$] (**5**), 1,2-bis-dithiarsolan-2-ylmercapto-ethane [$\text{As}_2(\text{SCH}_2\text{CH}_2\text{S})_2(\text{SCH}_2\text{CH}_2\text{S})$] (**6**) and tris-(pentafluorophenylthio)-arsen [$\text{As}(\text{SC}_6\text{F}_5)_3$] (**7**). The geometry around As for these compounds is best described as trigonal pyramidal with varying degrees of distortion. Compound **1** crystallizes in two polymorphic forms with similar structural parameters. The compounds have been characterized by IR, ^1H , ^{19}F , and ^{13}C NMR, X-ray crystallography and GC–MS.

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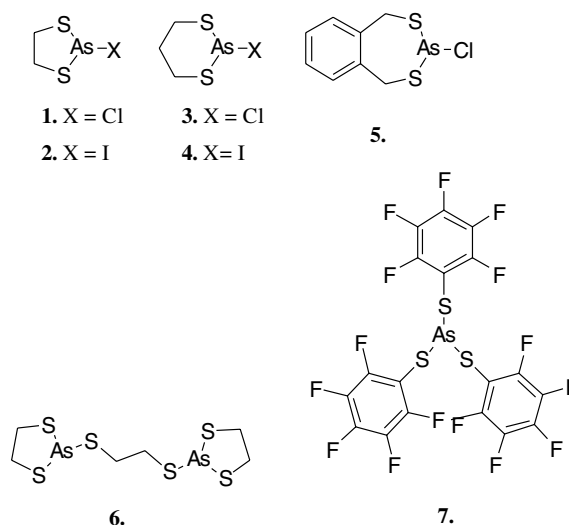
Keywords: Arsenic dithiolates; Bent's rule; Anomeric effect; Single crystal X-ray structure

1. Introduction

There has been an interest in the 2-halo-1,3,2-dithiarsolanes and their derivatives since the use of Lewisite ($\text{Cl}_2\text{AsCH}=\text{CHCl}$) and similar toxic arsenic-containing warfare agents in World War II. The first paper on the disposal of Lewisite was published in 1946 in which a method was presented for the synthesis of 2-chloro-1,3,2-dithiarsolane [1]. The motivation for the synthesis of such compounds was the need for a safe way to dispose of Lewisite and other arsenic chlorides in the late 1940s and 1950s. 2-Chloro-1,3,2-dithiarsolane was synthesized according to Scheme 1.

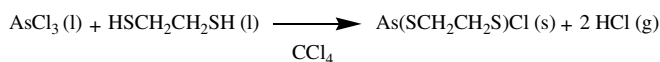
The synthetic route involves the formation of 2 equiv. of HCl gas, which can be used to monitor the progress of the reaction which goes to completion at room temperature.

A comprehensive study on the use of 1,2-bis-dithiarsolan-2-ylmercapto-ethane appeared in 1967 [2,3]. Since that time, the only work in this area was the use of arsenic dithiolates cations as carbene analogues [4,5] (Fig. 1).



With the exception of the crystal structure of 2-chloro-1,3,2-dithiarsolane (**1**) very little structural work has been accomplished. To remedy this situation, the present work details the crystal structures of 2-iodo-1,3,2-dithiarsolane

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Scheme 1. Synthetic route to 2-chloro-1,3,2-dithiarsolane.

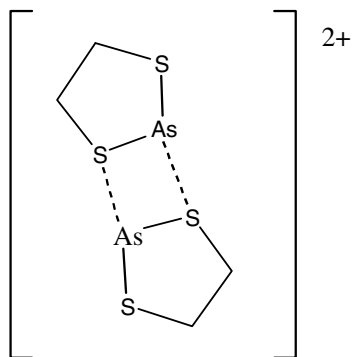


Fig. 1. Bis(1,3-Dithia-2-arsolidinium) cation as synthesized by Burford et al. [4].

(2), 2-chloro-1,3,2-dithiarsenane (3), 2-iodo-1,3,2-dithiarsenane (4), 3-chloro-4H,7H-5,6-benz-1,3,2-dithiarsepine (5), 1,2-bis-dithiarsolan-2-ylmercapto-ethane (6) and tris-(pentafluorophenylthio)-arsen (7) along with their complete characterization.

There are two fundamental characteristics demonstrated in these compounds. Bent's rule comes into play in terms of substituting different halides on the synthesized heterocycles. As the rule states: more electronegative substituents "prefer" hybrid orbitals with more "p" character, and more electropositive substituents "prefer" hybrid orbitals with more "s" character [6]. The more electronegative halide on the arsenic center induces more "p" character in the arsenic halide bond and as a result induces more "s" character in the remaining orbitals between arsenic and sulfur. To take advantage of the effect, we can allow for better orbital overlap with more electronegative groups with more "p" bias, if the sulfurs have more "s" character in the arsenic sulfur bond.

Also, the anomeric effect dominates placement of the terminal halides in these compounds. The consequence of the anomeric effect is that the electron-withdrawing groups adjacent to a heteroatom will have an axial preference. This is well established for six-membered rings and can be seen in the compounds reported here.

To the best of our knowledge the fluoro-analogue of 2-chloro-1,3,2-dithiarsolane has not been reported. In fact, there are few references to any group 15 fluoro-dithiols and the 2-fluoro-arsenic dithiolate moiety has not been reported [7,8]. The fluoro compounds are of interest since the arsenic-fluorine bond has the highest bond enthalpy at -318.3 kJ/mol in comparison with the rest of the arsenic trihalides [9].

The reason for the inability of an alkyl dithiol to form the fluoro-arsenic-dithiol can be described in hard-soft acid-base terminology. Based on the comparative softness of the $\text{As}^{(\text{III})}$ metalloid and the hard fluoride ligand, the

arsenic needs other hard ligands on it to mediate the hard-soft discrepancy of the arsenic center.

In order to provide a fundamental understanding of cyclized As-dithiolates, the IR, solution NMR, X-ray crystallography and GC-MS characterization data is described.

2. Experimental

Caution. Arsenic compounds are toxic and should be handled with care.

2.1. General methods

AsCl_3 was purchased from Alfa Aesar. AsF_3 was purchased from SynQuest Labs. Both AsCl_3 and AsF_3 are highly toxic and carcinogenic and must be handled and disposed of as hazardous materials. The dithiols obtained from Aldrich were used as delivered without further purification. All manipulations were carried out using standard inert atmosphere techniques under a nitrogen atmosphere. NMR spectra were obtained at room temperature in CDCl_3 on Varian Gemini 200 or Varian Innova 400 NMR spectrometers. Chemical shifts are reported in ppm, relative to tetramethylsilane. ^{19}F spectra are referenced to A,A,A-trifluorotoluene.

FT-IR spectra were recorded as KBr pellets on a Varian Spec 9800. Melting points were obtained on a Mel-Temp melting point apparatus.

2.2. Preparation of 2-chloro-1,3,2-dithiarsolane (1a and 1b)

1,2-Dithioethane (2.39 g, 25.4 mmol) in 50 mL CCl_4 was added dropwise to arsenic trichloride (5.03 g, 28.0 mmol) in 50 mL CCl_4 at room temperature. The reaction was stirred for an hour and then moved to a freezer at -20 °C where 5.13 g of crystals formed overnight. The crystals were kept at -20 °C and the solution filtered off to obtain a yield of 97.9%. Mp: 38.5–39.0 °C. ^1H NMR (CDCl_3) δ : 3.77 (m, 4H). ^{13}C NMR (CDCl_3) δ : 44.63 (s). IR (ν , cm^{-1} , KBr): 3448 (m, br), 2951 (m), 2910 (m), 1722 (w), 1642 (w), 1409 (s), 1384 (m), 1281 (m), 1231 (w), 1144 (w), 1106 (w), 992 (w), 930 (m), 832 (s), 669 (w), 644 (w), 599 (w), 450 (w). Mass spectra (GC-MS): 202 ($\text{AsCl}(\text{SCH}_2\text{CH}_2\text{S})^+$), 167 ($\text{As}(\text{SCH}_2\text{CH}_2\text{S})^+$).

2.3. Preparation of 2-iodo-1,3,2-dithiarsolane (2)

Sodium iodide (0.75 g, 5.00 mmol) was dissolved in 20 mL of acetone and added dropwise to 2-chloro-1,3,2-dithiarsolane (1.01 g, 5.00 mmol) dissolved in 20 mL acetone at room temperature. A white precipitate formed and the solution turned red. The solvent was removed under vacuum to isolate an orange solid. This was recrystallized from $\text{CCl}_4/\text{CHCl}_3$ to yield 1.14 g of crystalline solid (78.0%). Mp: 74.0–74.5 °C. ^1H NMR (CDCl_3) δ : 3.81 (d, 4H). ^{13}C NMR (CDCl_3) δ : 46.07 (s). IR (ν , cm^{-1} , KBr): 3447 (m, br), 2960 (w), 2902 (w), 1628 (m), 1403 (m),

1277 (w), 1106 (w), 929 (w,sh), 827 (m), 664 (m), 445 (w). Mass spectra (GC–MS): 294 (AsI(SCH₂CH₂S))⁺, 167 (As(SCH₂CH₂S))⁺.

2.4. Preparation of 2-chloro-1,3,2-dithiarsenane (3)

1,3-Dithiopropane (2.75 g, 25.5 mmol) was dissolved in 25 mL of CCl₄ and added dropwise to a solution of arsenic trichloride (5.04 g, 27.1 mmol) in 25 mL CCl₄ at room temperature. The reaction was stirred for an hour and the solution cooled to –20 °C and kept at that temperature for 24 h at which point a white crystalline precipitate formed. The solution was filtered and the resulting solid dried completely, yielding 4.96 g of a crystalline solid in 90.0% yield. Mp: 40.5–41.0 °C. ¹H NMR (CDCl₃) δ: 3.50 (m, 2H), δ 3.06 (m, 2H), δ 2.27 (m, 2H). ¹³C NMR (CDCl₃) δ: 26.587 (s), 25.797 (s). IR (ν, cm⁻¹, KBr): 3448 (m, br), 2904 (m), 2820 (w), 2360 (w), 1635 (w), 1416 (s), 1338 (w), 1296 (m), 1269 (m), 1245 (m), 1179 (w), 1115 (w), 995 (w), 899 (w), 855 (w), 803 (w), 739 (w), 618 (m), 411 (w). Mass spectra (GC–MS): 216 (AsCl(SCH₂CH₂CH₂S))⁺, 181 (As(SCH₂CH₂CH₂S))⁺.

2.5. Preparation of 2-iodo-1,3,2-dithiarsenane (4)

Sodium iodide (0.75 g, 5.00 mmol) in 10 mL acetone was added to 2-chloro-1,3,2-dithiarsenane (1.08 g, 4.99 mmol) dissolved in 20 mL of acetone at room temperature. Both solutions were clear before addition. Upon addition, the solution took on a bright orange tint and a white precipitate formed. The white precipitate was filtered out and part of the solvent was removed from the solution under vacuum. The solution was then allowed to crystallize and 0.24 g of dark red orange crystals formed at –20 °C in a 15.6% yield. Mp: 45–46 °C. ¹H NMR (CDCl₃, ppm) δ: 3.24 (t, 4H), δ: 2.29 (p, 2H). ¹³C NMR (CDCl₃, ppm) δ: 31.14 (s), 26.95(s). IR (ν, cm⁻¹, KBr): 3448 (m, br), 2896 (m), 2832 (m), 2364 (w), 1627 (m), 1412 (s), 1364 (w), 1293 (w), 1265 (m), 1179 (w), 892 (w), 851 (w), 802 (w), 775 (w), 616 (w). Mass spectra (GC–MS): 308 (AsI(SCH₂CH₂CH₂S))⁺, 181 (As(SCH₂CH₂CH₂S))⁺.

2.6. Preparation of 3-chloro-4H,7H-5,6-benz-1,3,2-dithiarsine (5)

1,2-bis-Mercaptomethylbenzene (1.00 g, 5.87 mmol) was dissolved in 20 mL of CCl₄ and added dropwise to arsenic trichloride (1.20 g, 6.62 mmol) in 20 mL CCl₄ at room temperature. The reaction was stirred overnight and cooled to –20 °C and kept at that temperature for a week. Clear star-like crystals formed in the solution. The solvent was then removed yielding 1.57 g of a crystalline solid in a yield of 96.2%. Mp: 117–119 °C. ¹H NMR (CDCl₃, ppm): δ 7.17 (phenyl, m, 4H), δ 5.11 (CH₂, d, 2H), δ 3.934 (CH₂, d, 2H). ¹³C NMR (CDCl₃, ppm): δ 139.31, δ 130.51, δ 129.60 (–phenyl–), δ 33.20 (–CH₂–). IR (ν, cm⁻¹, KBr): 3448 (wb), 3055 (w), 3026 (w), 2964 (w), 2933 (w), 1643 (w),

1493 (s), 1440 (s), 1416 (w), 1385 (w), 1301 (w), 1236 (m), 1211 (w), 1185 (m), 1156 (w), 1073 (w), 949 (w), 860 (w), 828 (w), 766 (vs), 762 (s), 666 (s), 589 (m), 499 (m). Mass spectra (GC–MS): 243 (As(SCH₂)₂(C₆H₄))⁺, 168 ((SCH₂)₂(C₆H₄))⁺, 104 ((CH₂)₂(C₆H₄))⁺.

2.7. Preparation of 1,2-bis-dithiarsolan-2-ylmercapto-ethane (6)

2-Chloro-1,3,2-dithiarsolane (1.01 g, 5.00 mmol) was dissolved in 20 mL of THF and an aqueous solution of Na₂CO₃ (1.00 g, 9.43 mmol, in 60 mL H₂O) was added to form a white precipitate. The solution was stirred for 5 min and then filtered to isolate 0.379 g of a white precipitate in a yield of 53.4%. The precipitate was dissolved in a 50/50 solution of CHCl₃/CH₃OH and slowly evaporated to obtain X-ray quality crystals. Mp: 81.5–82.0 °C. ¹H NMR (CDCl₃) δ: 3.507 (m, 8H), δ 3.106 (s, 4H). ¹³C NMR (CDCl₃) δ: 42.722 (s), δ 35.890 (s). IR (ν, cm⁻¹, KBr): 3449 (b), 2947 (w), 2906 (s), 1594 (m), 1409 (s), 1275 (s), 1195 (s), 1110 (w), 991 (w), 929 (w), 831 (s), 720 (w), 679 (m), 645 (w), 451 (w). Mass spectra (GC–MS): 167 (AsSCH₂CH₂S)⁺.

2.8. Preparation of tris-(pentafluorophenylthio)-arsen (7)

Arsenic trifluoride (1.00 ml, 20.02 mmol) was dissolved in 5 mL of CCl₄ and pentafluorothiophenol (5.40 mL, 40.50 mmol) was dissolved in 20 mL of CCl₄. Upon slow addition of the two solutions, a white precipitate formed. The reaction was left stirring for 24 h under a N₂ atmosphere. The solvent was then removed and the precipitate was dissolved in a mixture of CH₂Cl₂, toluene, acetonitrile and trifluorotoluene in a 1:1:3:3 ratio. The solvent mixture was evaporated slowly to produce 9.068 g of X-ray quality crystals in a yield of 99.96%. Mp: 76–77 °C. ¹⁹F NMR (CDCl₃, ppm) δ –135.29 (m)(C–F *meta*), δ –153.35 (m)(C–F *para*), δ –164.27 (m)(C–F *ortho*). IR(ν, cm⁻¹, KBr): 1637 (m), 1488 (s), 1401 (w), 1377 (w), 1291 (w), 1093 (vs), 1019 (w), 980 (vs), 859 (vs), 723 (w), 634 (w), 417 (w). Mass spectra (GC–MS): 473 (As(SC₆F₅)₂)⁺, 274 (As(SC₆F₅))⁺.

2.9. X-ray crystallographic analysis

X-ray diffraction data were collected at 90 K on a Nonius Kappa CCD diffractometer unit using Mo K α radiation from colorless regular shaped crystals mounted in Paratone-N oil on glass fibers. Initial cell parameters were obtained using DENZO [10] from 1° frames and were refined via a least-square scheme using all data-collection frames (SCALEPACK) [10]. The structures were solved by direct methods (SHELXL-97) [11] and completed by difference Fourier methods (SHELXL-97) [11]. Refinement was performed against F² by weighted full-matrix least-square. Hydrogen atoms were placed at calculated positions using suitable riding models with isotropic displacement parameters

Table 1
Crystallographic data for compounds 1–3

	1a	1b	2	3
Empirical formula	C ₂ H ₄ AsClS ₂	C ₂ H ₄ AsClS ₂	C ₂ H ₄ AsIS ₂	C ₃ H ₆ AsClS ₂
Formula weight	202.54	202.54	293.99	216.57
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>Cc</i>	<i>Pnma</i>
<i>a</i> (Å)	9.7563(2)	6.63120(10)	9.9446(3)	9.9720(5)
<i>b</i> (Å)	7.09300(10)	9.3076(2)	9.8158(3)	9.7510(4)
<i>c</i> (Å)	9.2864(2)	9.6441(2)	13.6402(4)	7.0530(6)
α (°)	90.0	90.0	90.0	90.0
β (°)	111.9504(9)	90.0	100.1139(12)	90.0
γ (°)	90.0	90.0	90.0	90.0
<i>V</i> (Å ³)	596.05(2)	595.24(2)	1310.79(7)	685.81(7)
<i>Z</i>	4	4	8	4
Density (g cm ⁻³)	2.257	2.260	2.979	2.097
Absorption coefficient (mm ⁻¹)	6.702	6.712	10.400	5.833
Reflections collected	1979	1044	2775	2212
Unique reflections	1058	1044	2772	650
<i>R</i> ₁ ^a	0.0142	0.0161	0.0228	0.0267
<i>wR</i> ₂ ^a	0.0313	0.0395	0.0416	0.0621

^a Final *R* indices [*I* > 2σ(*I*)].

Table 2
Crystallographic data for compounds 4–7

	4	5	6	7
Empirical formula	C ₃ H ₆ AsIS ₂	C ₈ H ₈ AsClS ₂	C ₃ H ₆ AsS ₃	C ₁₈ AsF ₁₅ S ₃
Formula weight	308.02	278.63	213.18	672.28
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>Pnma</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>Fdd2</i>
<i>a</i> (Å)	7.3970(2)	9.5439(3)	5.09160(10)	32.52220(10)
<i>b</i> (Å)	12.9494(3)	9.9009(3)	10.2877(3)	46.8717(4)
<i>c</i> (Å)	8.0262(2)	10.4746(3)	26.2326(8)	5.5499(6)
α (°)	90.0	90.0	90.0	90.0
β (°)	101.1213(10)	90.0	90.0	90.0
γ (°)	90.0	90.0	90.0	90.0
<i>V</i> (Å ³)	754.37(3)	989.78(5)	1374.09(6)	8460.1(9)
<i>Z</i>	4	4	8	16
Density (g cm ⁻³)	2.712	1.870	2.061	2.111
Absorption coefficient (mm ⁻¹)	9.042	4.065	5.737	2.042
Reflections collected	3386	2155	2514	4794
Unique reflections	1735	1208	2514	4794
<i>R</i> ₁ ^a	0.0186	0.0231	0.0368	0.0349
<i>wR</i> ₂ ^a	0.0383	0.0503	0.0701	0.0853

^a Final *R* indices [*I* > 2σ(*I*)].

derived from their carrier atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters. Atomic scattering factors were taken from the International Tables for Crystallography volume C [12]. Details of crystal data, data collection, and structure refinement are listed in Tables 1 and 2. Table 3 lists selected bond lengths and bond angles. Hydrogen atoms are omitted for clarity in Figs. 1–5.

3. Results and discussion

The 2-halo-1,3,2-dithia arsenic compounds were synthesized according to Scheme 2. The synthetic route involves the formation of 2 equiv. of HCl gas or the formation of an insoluble salt as the driving force behind the reactions.

The reactions can be monitored by observing gas evolution or salt formation and go to completion at room temperature.

It is speculated that the five-membered ring is the least reactive in the series of *n* = 2, 3, and 4 in the alkylene linkage in AsX(S(CH₂)_{*n*}S) where X is the halide. This speculation arises from the ease with which the six-membered rings break upon addition of base and the inability to form and isolate the seven-membered ring compound under the reaction conditions. This contrasts with a previously postulated model, which states that larger rings should be more stable [13]. It should be mentioned that ease of formation and actual stability of the compounds are not equivalent. Conversely, there is no evidence to show that the dithiarsepane ring, if formed, is stable as such. The possibility of rearrangement into an oligomeric form seems most likely due

Table 3
Selected bond lengths (Å) and bond angles (°) for **1a**, **1b**, **2**, **3**, **4**, **5**, **6**, and **7**

	1a	1b	2^a	3	4	5	6	7
As(1)–S(1)	2.2402(5)	2.2083(6)	2.2119(19)	2.2188(9)	2.2252(7)	2.2317(5)	2.2315(17)	2.2660(10)
As(1)–S(#1)				2.2189(9)		2.2316(5)		
As(1)–S(2)	2.2088(5)	2.2271(7)	2.2311(17)		2.2215(7)		2.2472(16)	2.2622(11)
As(1)–X(1)	2.2669(4)	2.2528(7)	2.6502(7)	2.2328(13)	2.6036(3)	2.2351(8)		
As(1)–S(3)							2.2610(17)	2.2585(10)
As(2)–S(4)							2.2683(16)	
As(2)–S(5)							2.2311(16)	
As(2)–S(6)							2.2452(16)	
S(1)–As(1)–S(#1)				102.20(5)		105.06(3)		
S(1)–As(1)–S(2)	93.398(18)	93.91(3)	93.20(7)		101.42(3)		93.24(6)	87.82(4)
S(1)–As(1)–X(1)	97.445(18)	99.19(3)	99.80(5)	98.32(3)	100.87(2)	97.842(19)		
S(#1)–As(1)–X(1)				98.32(3)		97.842(19)		
S(2)–As(1)–X(1)	98.857(17)	97.91(3)	100.56(5)		100.624(19)			
S(1)–As(1)–S(3)							102.15(6)	98.31(4)
S(2)–As(1)–S(3)							94.33(6)	98.53(4)
S(4)–As(2)–S(5)							99.46(6)	
S(4)–As(2)–S(6)							93.21(6)	
S(5)–As(2)–S(6)							93.86(6)	

^a In **2** only one molecule (A) of the unit cell is reported.

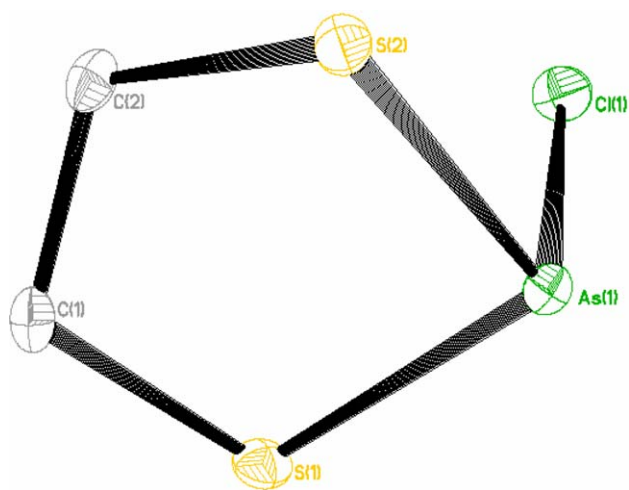


Fig. 2. Thermal ellipsoid plot (50%) of 2-chloro-1,3,2-dithiarsolane (**1a**).

to the mass spectral data obtained from failed attempts at the synthesis of the dithiarsepane. After several attempts, 2-chloro-1,3,2-dithiarsepane was not successfully isolated

and characterized. When arsenic trichloride and 1,4-dithiobutane are combined at room temperature a white emulsion forms which when extracted into a CS₂, gives much higher molecular weight species.

Preliminary results indicate that the As–S bonds in cyclized halo arsenic dithiolates are acid stable but undergo salt eliminations and redistribution under basic conditions. Certain combinations of chelate length and change in halide lead to breakage of the chelate As–S bonds in the salt elimination process.

The truncated As–S bonds shown in these compounds (bond lengths within the sum of the covalent radii) and the slightly elongated bond lengths of the arsenic halides indicate the effects of unequal orbital hybridization as called for in Bent's rule. Unfortunately, the variances in bond lengths are inconclusive due to experimental error. Compounds **1–5** all display an axial alignment of the halide on the arsenic center with respect to the ring.

The combination of arsenic(III) oxide with 1,2-ethanedithiol and thioglycol results in the formation of the heterocyclic thioesters, As₂(SCH₂CH₂S)₂(SCH₂CH₂S) and

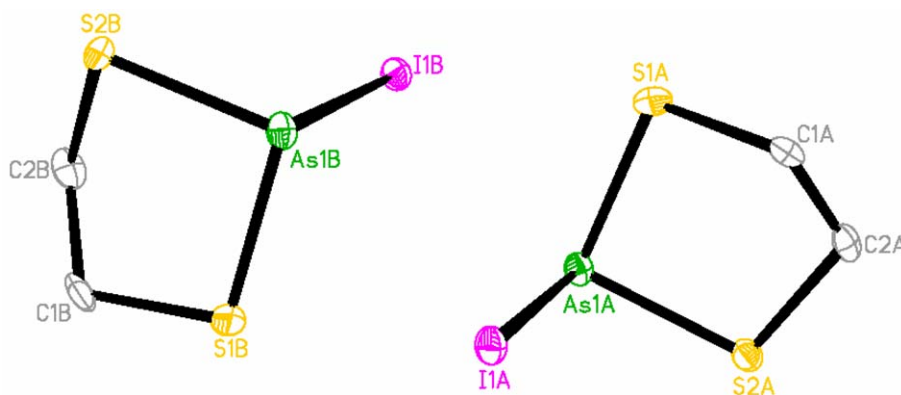


Fig. 3. Thermal ellipsoid plot (50%) of 2-iodo-1,3,2-dithiarsolane (**2**).

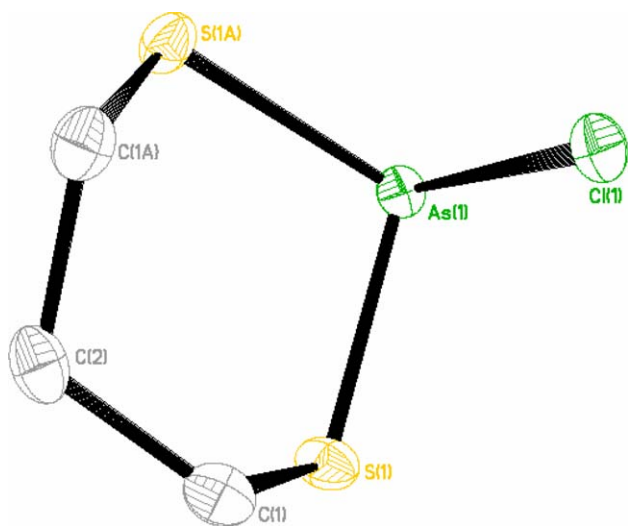


Fig. 4. Thermal ellipsoid plot (50%) of 2-chloro-1,3,2-dithiarsenane (**3**).

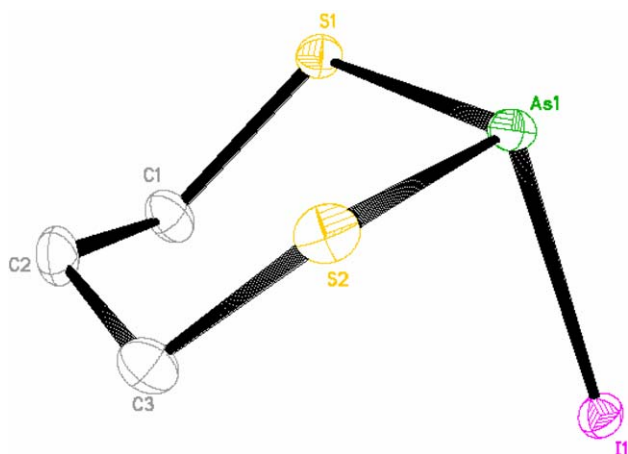
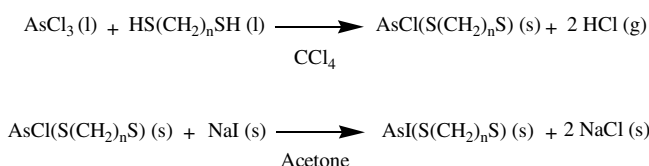


Fig. 5. Thermal ellipsoid plot (50%) of 2-iodo-1,3,2-dithiarsenane (**4**).



Scheme 2. Examples of synthetic routes to various 2-halo-1,3,2-dithia arsenic compounds.

$\text{As}_2(\text{SCH}_2\text{CH}_2\text{O})_2(\text{SCH}_2\text{CH}_2\text{O})$, which when combined with arsenic trihalides form the ester halides. It has been reported that **1a**, when dissolved in a polar solvent (dichloromethane), dissociates and as such allows for exchange of the chlorine on the arsenic center [2]. However, in the absence of As–S bond cleavage, dimeric structures result [14]. Under various conditions, **1** can be crystallized in the monoclinic space group $P2_1/c$ as **1a** or in the orthorhombic space group $P2_12_12_1$ as **1b**. The bond lengths and angles for the two crystalline polymorphs are the same. For example,

in the orthorhombic $P2_1/c$ space group the variance in bond lengths between As and S on the same molecule is approximately 0.0314 Å whereas in the $P2_12_12_1$ space group the As–S bonds have a variance of approximately 0.0188 Å. These values lie within or are extremely close the value of 0.02 Å, which is the limit for experimental error in the single crystal X-ray structure determination.

The X-ray structure of **1a** has been previously reported [4,15]. However, the crystals were crystallized in the monoclinic space group $P2_1/c$, whereas **1b** was crystallized in the orthorhombic space group $P2_12_12_1$. This was achieved by changing the reaction conditions. Compound **1a** was dissolved in CCl_4 and a molar equivalent of benzyl alcohol added and then recrystallized as orthorhombic **1b**. The alcohol clearly influenced the crystallization but does not appear in the structure.

The ^1H NMR spectrum of **1** shows a multiplet (3.77 ppm) for the ethylene protons in the backbone. The ^{13}C NMR spectrum shows a singlet (44.63 ppm) for the backbone carbons. It can be concluded that there is only one magnetic environment for the backbone carbons. The IR spectrum for compound **1** is strikingly similar in compounds **2–6**. The C–S stretches at 669 and 644 cm^{-1} and As–S stretch at 450 cm^{-1} are indicative of the presence of a ring [16,17].

Compound **2** contains two molecules in its asymmetric unit and crystallizes in the monoclinic space group Cc . The bond lengths and angles are very similar to **1a** and **1b** as seen in Table 3. Thus, varying the terminal halide seems to have little effect on the bond angles and distances in the halo-dithiarsolanes. However, the distance between I(1)B to S(2)A is 3.745 Å in the packing diagram and as such is within the sum of the Van der Waals radii for I and S at 3.78 Å. The slightly shortened distances are likely due to the packing within the unit cell. However, the As(1A)–I(1A) distance is 2.65 Å which when compared to the sum of the covalent radii (2.54 Å) is longer indicating a more ionic bond.

The ^1H NMR spectrum of **2** shows a doublet (3.81 ppm) for the ethylene protons in the backbone. The ^{13}C NMR spectrum shows a singlet (46.07 ppm) for the backbone carbons. Just as in **1**, it can be concluded that there is only one magnetic environment for the backbone carbons. Some of the spectroscopic data reported here does not match the published data available for **2** [16,18]. In particular, the ^1H NMR signal at 3.81 ppm differs considerably from the published value of 3.00 ppm. This could be due to solvent effects and improvements in NMR hardware. Also, the IR spectrum shows the characteristic C–S and As–S stretches (664 and 445 cm^{-1}).

Compound **3** crystallizes in the orthorhombic space group $Pnma$. The bonding angle between S–As–S is 102° which is considerably wider than in the five-membered rings. However, this has little effect on the As–S bond length (2.22 Å). Thus, there are no strong distortions in five or six membered rings.

In the unit cell, the intermolecular arsenic hydrogen distances are around 3.02 Å, while the chlorine hydrogen

distances are around 2.90 Å. Both of these values are within the sum of the Van der Waals radii (3.05 and 2.95 Å) of the respective atoms.

There are three multiplets (3.50, 3.06 and 2.27 ppm) for the hydrogens on the propylene carbons, which are similar to the previously reported values of (3.43, 2.76, and 1.85 ppm). The differences can be attributed to the use of different NMR solvents (CDCl₃ versus C₆D₆) [19]. The fact that there are three ¹H NMR signals is due to the axial and equatorial signals from the protons on C1 and C(1A) and a multiplet due to the protons on C2. Pyramidal inversion is possible at the arsenic but with a high energetic barrier (25–42 kcal/mol), the inversion is slow [20,21]. This explains the three distinct multiplets seen in the ¹H NMR.

The IR spectrum shows the C–S stretch (618 cm⁻¹) and As–S stretch (411 cm⁻¹).

Compound **4** crystallizes in the monoclinic space group *P*2₁/*n*. The iodine atom seems to have little effect on the bond angles of the molecule versus the chlorine analogue. In the solid state, the iodine does seem to gently break the symmetry of the molecule whereas the chlorine analog maintains a higher level of symmetry with a σ_v (vertical mirror plane) passing through the middle of the molecule and containing the chlorine. This could be due to larger displacement of the iodine atom and a slight shift of the iodine away from the symmetry axis. The As–S bonds are slightly elongated and the angles between S–As–X are widened by 2.4° more in the iodo complex but the S–As–S bond angle is slightly smaller in the iodo complex, 102.20° versus 101.42° in the iodo analogue. The rings are not affected by the identity of the terminal halide. This explains the spectroscopic similarity between **1**, **2**, and **6** and between **3** and **4**. The ¹H NMR shows a triplet and a pentet (3.24, 2.28 ppm) for the hydrogens on the propylene backbone. The ¹³C NMR shows two singlets (31.14,

26.95 ppm) which correspond to the “*ortho* and *para*” positions, respectively. The IR spectrum shows the C–S stretch (616 cm⁻¹) but the As–S stretch is not observed. This is most likely due to the band falling very close to the edge of the range of the instrument (400 cm⁻¹). The spectroscopic data are consistent with what is expected based on the IR, ¹H and ¹³C NMR of the chloro analogue. There has been some interest in this particular compound in radioarsenic labeling where an ⁷²As atom would be used as a positron emitter [22] (see Fig. 6).

Compound **5** crystallizes in the orthorhombic space group *Pnma*. The chosen route to obtain a seven membered arsenic dithiolate ring involves “locking” the backbone of the arsepane to form the heterocycle. The S–As–S bond angle in **5** demonstrates the strain by having the largest angle seen thus far at 105°.

The spectroscopic data obtained matches well with the published information available for **5** [23]. The ¹H NMR show the phenyl hydrogens (7.17 ppm), and methylene hydrogens (5.11, 3.93 ppm). The methylene hydrogens are in different magnetic environments and are split. This is due to the anomeric effect. Two of the hydrogens on the methyl groups are closer to the chlorine and are in different environments. The ¹³C NMR shows the carbon in the phenyl ring (139.31, 130.51, 129.60 ppm) and the methyl carbons (33.20 ppm). In the IR spectrum, the strong bands (766, 661 cm⁻¹), which indicate an anti-symmetric stretch between carbon and sulfur and a symmetric stretch, respectively, are of note. This is unusual because these bands are usually weak and the anti-symmetric band is rarely observed. The AS–S stretch is shifted higher than seen in the other compounds (499.77 cm⁻¹). A similar compound was reported previously and uses the toluene dithiol moiety to bind to the arsenic center [24]. However, the actual S–As–S ring structure resembles more what is found in **1**.

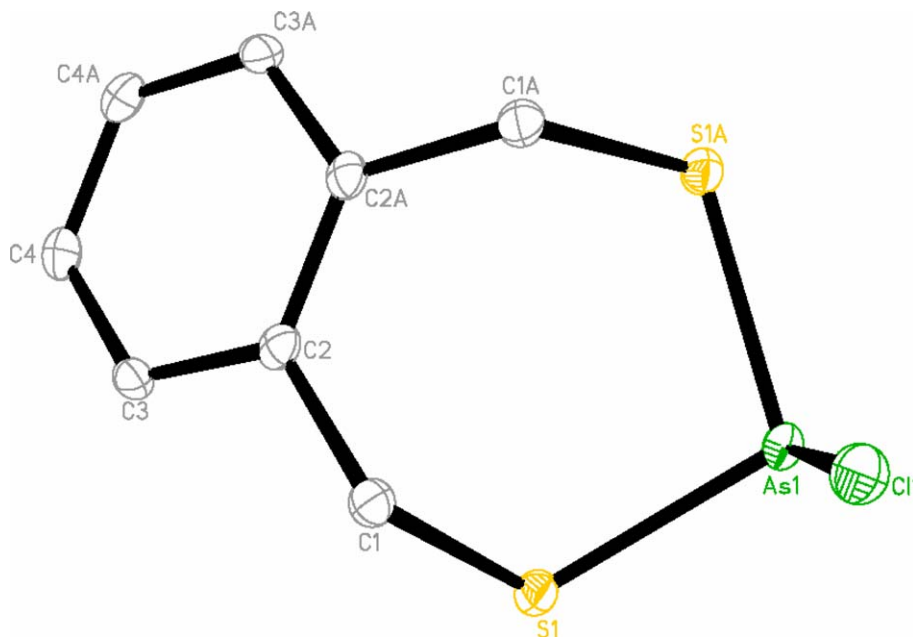


Fig. 6. Thermal ellipsoid plot (50%) of 3-chloro-4H,7H-5,6-benz-1,3,2-dithiarsepine (**5**).

There are no π -stacking affects in the structure of **5**. The arsenic and backbone carbons are approximately 3.55 Å apart which causes the lone pair of the arsenic to be centered directly over the phenyl ring.

Compound **6** crystallizes in the orthorhombic space group $P2_12_12_1$. The As–S bond lengths range from 2.23–2.28 Å and the S–C bond lengths are around 1.81–1.84 Å. These are typical As–S and S–C bond lengths. However, there is a narrowing of the bond angle between S1–As1–S2 and S5–As2–S6 in compound **6** and the angle made with the sulfur located on the linkage. The constriction is approximately 6° with a range from 93° to 102°. Consequently, the five membered rings do not force a severe skewing of the orbitals involved in bonding (see Fig. 7).

Compound **6** seems to be the preferred product in reactions involving ring breakage of five membered rings. This is due to the stability of the trithioarsenic moiety versus a halo arsenic dithiolate species.

This stability was also seen in the pharmacological attributes of nonalkylating arsenicals [25]. It was previously postulated that the 2-chloro-1,3,2-dithiarsolane is first hydrolyzed at the As–Cl bond followed by breakage of the As–S bond by water, which then provides a free sulfhydryl group which can react with another equivalent of **1** to eliminate HCl [1]. However water does not seem to be the only solvent that will function successfully to break the As–S bond.

The ^1H NMR spectrum shows a multiplet (3.51 ppm), which arises from the ethylene hydrogens in the ring, and a singlet (3.11 ppm), which is due to the bridging ethylene hydrogens. There are two signals in the ^{13}C NMR spec-

trum, a singlet due to ethylene carbons in the ring (42.72 ppm) and a singlet due to the bridging ethylene carbons (35.89 ppm). The IR spectrum shows three bands which represent the A'' ring C–S stretch (679 cm^{-1}), A' ring C–S stretch (645 cm^{-1}) and A' As–S ring deformation (451 cm^{-1}). These are similar to the published values [25] (see Fig. 8).

Compound **7** crystallizes in the orthorhombic space group $Fdd2$. This compound was synthesized to determine the bond length of the As–S bonds in the absence of a ring structure yet retaining the electron-withdrawing power of a pseudo-halide. It was thought that the addition of large electron withdrawing groups would strengthen the As–S bond and thus shorten it. Nonetheless, **7** exhibits very similar As–S bonds to those in **6**. This either negates the strength of the pentafluorophenylthio group as an electron-withdrawing group or equates it to a bond found in the cyclized arsenic dithiolates.

The angles around the arsenic center are somewhat unexpected. Two of the angles lie in the region of 98.3°–98.5° whereas one is significantly more acute at 87.8°. It is possible that the lone pair is inducing unequal sharing of the bonding orbitals involved. The bond lengths between the arsenic center and the different sulfurs vary from one another by only 0.06 Å.

The ^{19}F NMR shows the fluorines in the meta, para, and ortho positions on the phenyl rings (–135.29, –153.35, –164.27 ppm), respectively. The IR spectrum obtained indicates an aromatic C–C stretch (1489 cm^{-1}), C–F stretches (1094 cm^{-1} , 980 cm^{-1}), a C–S stretch (860 , 635 cm^{-1}), and an As–S stretch (417 cm^{-1}).

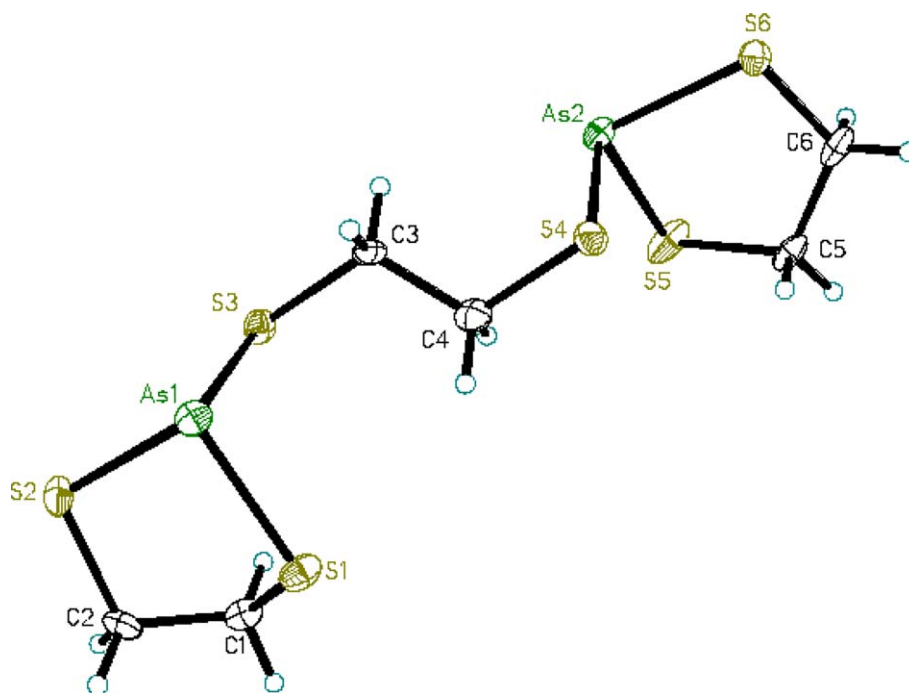


Fig. 7. Thermal ellipsoid plot (50%) of 1,2-bis-dithiarsolan-2-ylmercapto-ethane (**6**).

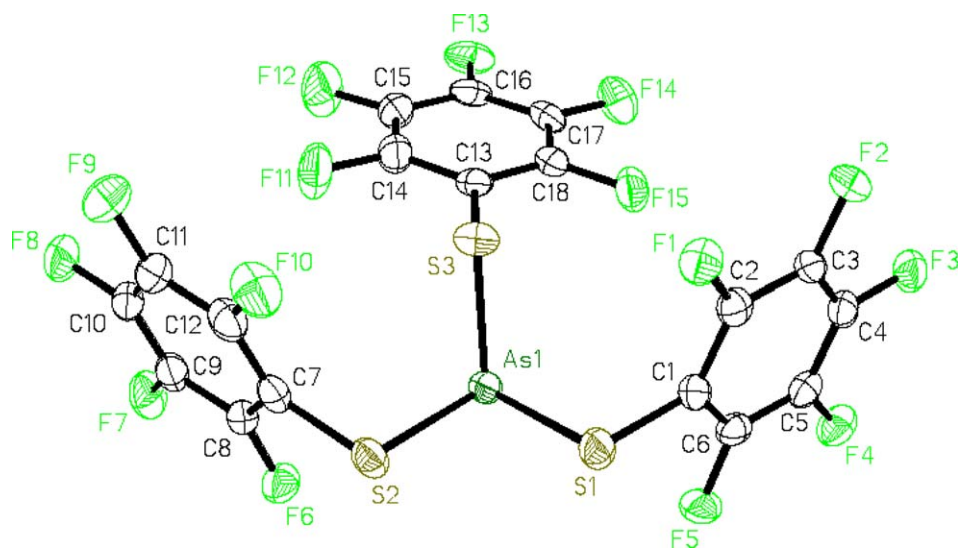


Fig. 8. Thermal ellipsoid plot (50%) of tris-(pentafluorophenylthio)-arsen (7).

Compound **7** has been used to make various metal complexes [26,27]. However, only the elemental analysis data and the melting point were reported previously.

4. Conclusion

This work provides new information on cyclized arsenic dithiolates, for which little characterization data was available. The bonding trends in the compounds can be explained by the anomeric effect and Bent's rule. The compounds shown here give a basis for future comparison of novel structural analogues.

5. Supporting information available

X-ray crystallographic files (CIF) CCDC 276894–276899 and CCDC 277012 contain the supplementary crystallographic data for this paper. These files can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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