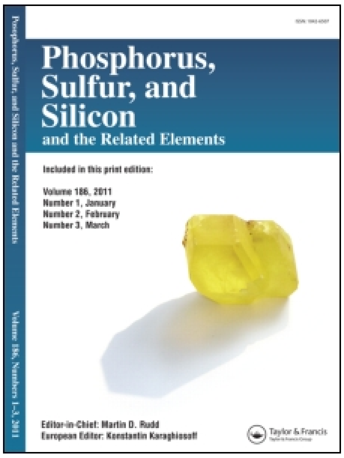

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REACTIONS OF ARSINIC AND ARSONIC ACIDS WITH H_2S AND H_2Se: CRYSTAL STRUCTURE OF 1,4-DIPHENYL-1,4-DIARSA-2,3,5-TRISELENACYCLOPENTANE

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REACTIONS OF ARSINIC AND ARSONIC ACIDS WITH H_2S AND H_2Se: CRYSTAL STRUCTURE OF 1,4-DIPHENYL-1,4-DIARSA-2,3,5-TRISELENACYCLOPENTANE

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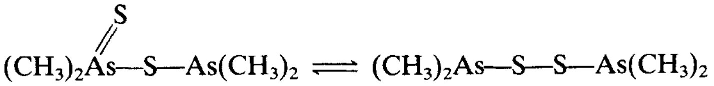
The reactions of a series of arsinic and arsonic acids with hydrogen sulfide and hydrogen selenide have been investigated. The various arsinic acids were found to produce a variety of products, but the reaction was characterized by the reduction of arsenic(V) to arsenic(III), loss of hydroxyl groups bonded to arsenic and, to a lesser degree, the rupture of arsenic-carbon bond(s). Phenylcarboxymethylarsinic acid yielded, on reaction with H_2S or H_2Se, 1,4-diphenyl-1,4-diarsa-2,3,5-trichalocogenapentanes, where the chalcogen atom is S or Se. Arsonic acids yielded as final products compounds having a range of stoichiometries ranging from RAsS to $R\cdot 7As_2S_3$. 1,4-Diphenyl-1,4-diarsa-2,3,5-triselenacyclopentane consists of a non-planar, five-membered ring in which the As—C bond distances are 1.962 Å, the As—Se bond distances are 2.388 Å and the Se—Se bond distance is 2.334 Å. The bond distances are very close to those which are expected for single, covalent bonds.

KEYWORDS Arsinic acids Arsonic acids Hydrogen sulfide Hydrogen selenide Arsenic heterocyclics Selenium heterocyclics

INTRODUCTION

In a study published in 1971,[1] we reported that the ^1H n.m.r. spectrum observed for the methyl protons in tetramethyldiarsine disulfide was not consistent with the single molecular form observed in the crystal structure.[2] Temperature dependent ^1H n.m.r. and infrared spectral studies suggested that in solution, the following equilibrium exists.



$$(CH_3)_2\overset{S}{\overset{\|}{As}}—S—As(CH_3)_2 \rightleftharpoons (CH_3)_2As—S—S—As(CH_3)_2$$

In order to understand this type of equilibrium in greater detail it was decided to study the ^1H n.m.r. spectrum of an analogue of the type $[Ar—As(R)]_2S_2$ in which the protons of the Ar and R groups would have widely separated proton chemical shifts. In this manner the proton resonances could be more easily monitored. However, when phenylcarboxymethylarsinic acid was treated with H_2S, the major product, easily and reproducibly isolated, was 1,4-diphenyl-1,4-diarsa-2,3,5-trithiacyclopentane. This unexpected observation caused us to investigate the reactions of a number of arsinic and arsonic acids with hydrogen sulfide and hydrogen selenide.

RESULTS AND DISCUSSION

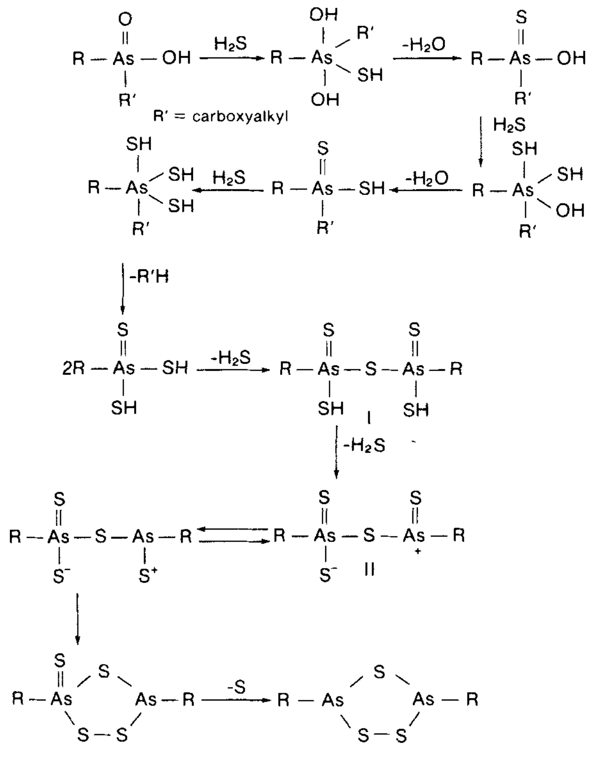
When an excess of gaseous hydrogen sulfide was passed through a solution of a phenylcarboxymethylarsinic acid, a solid separated from the solution which was unequivocally identified as 1,4-diphenyl-1,4-diarsa-2,3,5-trithiacyclopentane. This compound was previously reported by Schulte[3] as a product of the reaction between phenylarsonic acid and hydrogen sulfide in ammoniacal solution. In attempts to isolate some intermediates, the reaction between phenylcarboxymethylarsinic acid and various stoichiometric amounts of hydrogen sulfide (generated by the reaction of HCl with known amounts of Na_2S) was investigated. At molar ratios of arsinic acid/H_2S of 1:1, only the starting material was isolated; at a ratio of 1:2 a mixture of the starting material and cyclic product was obtained, and at ration of 1:3 to 1:15, the only product obtained was the cyclic derivative.

The reaction between phenyl-α-carboxyethylarsinic acid and hydrogen sulfide yielded the identical cyclic compound. In both cases, displacement of the carboxymethyl and carboxyethyl groups was confirmed by the identification of acetic and propionic acids in the solutions in which the reactions had been carried out.

The reaction between phenylcarboxymethylarsinic acid and excess hydrogen selenide also gave, as the only identifiable product, 1,4-diphenyl-1,4-diarsa-2,3,5-triselenacyclopentane. The absolute identification of this product was furnished by single crystal x-ray analysis. The reaction between phenylcarboxymethylarsinic acid and benzenethiol also took place with displacement of the carboxymethyl group. From this reaction, phenylbis(benzenethio)arsine was easily isolated and identified along with the oxidation product, diphenyl disulfide.

All of the foregoing suggest a mechanism for the formation of the cyclic product which is patterned after that suggested by Cullen and co-workers.[4] The mechanism, in principle, involves the addition of H_2S to form a pentacoordinate intermediate which undergoes the loss of water (Scheme I). This process is driven primarily by the thermodynamic stability of water and the stability of the arsenic-sulfur bond. This process is repeated and species are formed which, at some stage must involve the loss of carboxyalkyl groups as the acids. Two moles of the thioarsinic acid can condense by loss of H_2S to give rise to an As—S—As bonded intermediate (I). Loss of H_2S by (I) would give rise to (II), which can exist in the appropriate resonance forms and which, with loss of sulfur and concurrent reduction of arsenic(V) to arsenic(III) gives rise to the cyclic product.

Because of the objection of one of the reviewers of this paper to the postulated formation of (unstable?) geminal dithiols, an alternate pathway (suggested by the

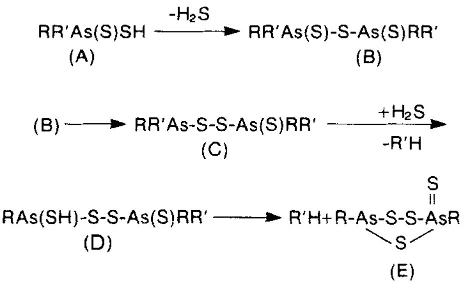


Scheme I

reviewer) is given in Scheme II. Intermediate E is identical with the penultimate one of Scheme I.

Examination of Table I shows that the formation of a compound having the stoichiometry $R_2As_2X_3$ is not uncommon. Such compounds are obtained by the reactions of phenylarsonic acid, *p*-aminophenylarsonic acid (X=Se), *p*-nitrophenylarsonic acid, *p*-chlorophenylarsonic acid (X=Se) and 2,4-dichlorophenylarsonic acid. While these compounds probably may have the 1,4-diarsa-2,3,5-trichalcogenacyclopentane structure, no definitive conclusions can be reached in the absence of structural data. The formation of $R_2As_2S_5$ from the reaction of *p*-methylphenylcarboxymethylarsinic acid with hydrogen sulfide suggests a cyclic diarsatrithiacyclopentane structure with the arsenic atoms in a pentavalent state, each bonded to a second sulfur atom. The mass spectrum of this compound yields, as the heaviest ion, that corresponding to $R_2As_2S_3$. The fragmentation pattern is very similar to that of $(C_6H_5)_2As_2S_3$ giving easily identifiable peaks corresponding to the fragments $C_7H_7AsS_3$, C_7H_7As, AsS and C_7H_7. The infrared spectrum of this compound shows an additional band at 580 cm^{-1} (not present in the spectrum of the trisulfide) which can be attributed to an As=S double bond.[5] The two doubly bonded sulfur atoms appear to be easily cleaved upon electron impact. The observations are consistent with a cyclic structure in which each pentavalent arsenic atom has the additional bond to sulfur.

Arsenic sulfides and selenides having a number of other stoichiometries were



Scheme II

also formed. No definitive statements about the structures of these compounds can be made, but when compounds having similar stoichiometries have been reported in the literature and structural data are available, it is probable that the compounds isolated in the present studied have similar structures.

o-Chlorobenzylarsonic acid undergoes reaction with hydrogen selenide with the formation of a compound having a stoichiometry RAsSe. Compounds of such a type are not unusual.[6,7,8] All experimental data suggests a polymeric structure,

TABLE I

Summary of products obtained from reactions of various arsinic and arsonic acids with H_2S or H_2Se

Substrate	Reactant H_2X $X=$	Major product[a]	Method of identification[b]
$RR_1As(O)OH$			
a. $R = p\text{-}CH_3C_6H_4$	S	cyclic $R_2As_2S_5$	anal., m.s., i.r.
$R_1 = H_2CCOOH$			
b. $R = C_6H_5$	Se	starting material	
$R_1 = CH_3$	S	$(R_1R_2As)_2S_2$	m.s.
$RAs(O)(OH)_2$			
c. $R = C_6H_5$	S	cyclic $R_2As_2S_3$	anal., m.s., m.m.p.
d. $R = p\text{-}CH_3C_6H_4$	S	$RAs_{14}S_{21}$	anal., m.s.
$p\text{-}CH_3OC_6H_4$		m.p., >300	
e. $R = p\text{-}NH_2C_6H_4$	S	$R_2As_3S_4$	anal., m.s.
		m.p., 125–130	
	Se	(cyclic?)$R_2As_2Se_3$	anal., i.r., m.s.
		m.p., dec. 140	
f. $R = p\text{-}NO_2C_6H_4$	S	(cyclic?)$R_2As_2S_3$	anal., i.r., m.s.
		m.p., 135–140	
g. $R = p\text{-}ClC_6H_4$	S	$RAsS_2$	anal.
	Se	(cyclic?)$R_2As_2Se_3$	anal.
		m.p., 123–125 dec.	
h. $R = p\text{-}ClC_6H_4CH_2$	S	R_2As_2S	anal., i.r.
	initially in NaOH	m.p., 123–125	
i. $R = o\text{-}ClC_6H_4CH_2$	Se	RAsSe	anal., i.r., m.s.
		m.p., 120–123	
j. $R = 2,4\text{-}Cl_2C_6H_3CH_2$	Se	$R_2As_2Se_3$	anal., i.r., m.s.
		m.p., 120–123	

[a] All mp are in °C.

[b] Anal., elemental analysis for C, H, As and chalcogen; m.s., low resolution mass spectrometry; m.m.p., mixed melting point with authentic sample; i.r., infrared. All of the original data are published in Reference 16.

$[RAsX]_n$ where $n \geqslant 2$. Bergerhoff and Namgung have reported on the structure of $(C_6H_5AsS)_4$. It consists of staggered eight-membered rings, $[(As{-}S)_4]$, stacked like coins.

A single compound having the stoichiometry R_2As_2S was formed by the reaction of *p*-chlorobenzylarsonic acid with hydrogen sulfide. A structure having a six-membered $(As_2S)_2$ ring seems reasonable with the As—R bond remaining intact. The formation of $R_2As_3S_4$ (R═*p*-aminophenyl) is interesting because such a reaction requires the cleaage of a carbon–arsenic bond. Arsenic–carbon bond cleavage is further illustrated by the formation of $RAs_{14}S_{21}$ where $R = p\text{-}CH_3C_6H_4$ or $p\text{-}CH_3OC_6H_4$. This appears to be an extended arsenic trisulfide structure in which a small number of As—R groups are retained. In the case of the reaction between phenylmethylarsinic acid and hydrogen sulfide, mass spectral data suggest the formation of $[C_6H_5(CH_3)As]_2S_2$. This appears to be a molecule of the type obtained by the reaction between dimethylarsinic acid and hydrogen sulfide,[1,2] but it was never isolated in pure form.

The nature of the products formed by the reactions between arsinic or arsonic acids with hydrogen sulfide or hydrogen selenide do not follow a predictable course. Certain patterns do appear to be consistent. These include the reduction of arsenic(V) to arsenic(III), the displacement of arsenic–oxygen bonds by arsenic–sulfur (or selenium) bonds and to a lesser extent, the rupture of arsenic–carbon bonds. The reaction is very probably thermodynamically driven, primarily by the formation of water, but also because arsenic–sulfur or –selenium bonds have been shown to be more hydrolytically stable than arsenic–oxygen bonds.[10] The mechanism proposed by Cullen and co-workers[4] is a reasonable one, and explains the formation of the observed products.

EXPERIMENTAL SECTION

Proton n.m.r. spectra were recorded on a Varian EM 390 spectrometer using tetramethylisilane as the internal standard. Solvents used were deuterium oxide, perdeuterated chloroform, or trifluoroacetic acid. Infrared spectra were recorded on a Sargent-Welch Pye Unicam 3-200 spectrometer. The region below 600 cm^{-1} was scanned using a Perkin Elmer model 283 B spectrometer. Samples were run in chloroform using cesium iodide cells or as potassium bromide pellets. Mass spectra were measured using the Kratos MS 50 mass spectrometer. Acetic and propionic acids were identified by gc/ms. Retention times were compared with those of authentic samples and experimentally separated fractions were co-chromatographed with authentic samples. A Hewlett-Packard model 5992-B spectrometer was used for this purpose.

Elemental analyses were performed by the Galbraith Laboratory, Inc., Knoxville, Tennessee.

Phenylarsonic acid, chloroacetic acid, hypophosphorous acid and sodium arsenite were purchased from the Aldrich Chemical Co. *p*-Nitrophenylarsonic acid, and *p*-aminophenylarsonic acid were furnished as gifts by the Salsbury Laboratories, Charles City, Iowa. *p*-Chlorophenylarsonic acid was purchased from Pfaltz and Bauer, Inc., Waterbury, Connecticut.

Hydrogen sulfide, contained in laboratory bottles, was purchased from the Fisher Scientific Co. Hydrogen selenide was generated by the reaction between dilute hydrochloric acid and aluminum selenide.

The other arsonic acids used in this study were synthesized according to the methods described by Starkey[11] and Ruddy.[12] A procedure described by Barker *et al.*[13] was used to prepare the necessary dichloroarsines. Phenylcarboxymethylarsinic acids were prepared in the manner described by Quick and Adams.[14] Methylphenylarsinic acid was synthesized using the method of Cragoe and co-workers.[15]

Phenyl-α-carboxyethylarsinic acid has not been previously reported. A solution containing 12.3 g, 113 mmol of α-chloropropionic acid in 11 ml of water containing 4.5 g of sodium hydroxide solution was added slowly, with stirring, to a solution prepared by dissolving 19.1 g 86 mmol of phenyldichloroarsine in 39 ml of water containing 15.5 g of sodium hydroxide. The combined solutions were stirred for 3 h at room temperature. The reaction mixture was neutralized by the addition of concentrated hydrochloric acid, filtered, and the filtrate made acid to Congo Red by the further addition of the acid. Cooling of the acidified filtrate caused the separation of the desired compound. Recrystallization from hot water afforded colorless crystals melting at 165–168·C. Anal.: calc'd (found); C, 41.88 (41.95); H, 4.30 (4.50); As, 29.03 (28.78); ([$^2H_6$]DMSO) 7.6 (aromatic protons), 4.3 (q, 1H, CH), 2.0 (d, 3H, CH_3); pK_1, 3.26; pK_2, 7.45 (measured from pH at half-equivalence point).

The following procedure, typical of those followed, describes the preparation of 1,4-diphenyl-1,4-diarsa-2,3,5-trithiacyclopentane. A solution containing 2 g (8.2×10^{-3} mole) of phenylcarboxymethyl arsinic acid in 25 ml. of warm absolute ethanol was prepared. The solution was cooled to room temperature and a stream of hydrogen sulfide gas was bubbled through the solution for one h. The precipitate of elemental sulfur ((recrystallized from CS_2 and identified by mp and mass spectroscopy) was removed by filtration. On cooling, the ethanol filtrate yielded crystals of 1,4-diphenyl-1,4-diarsa-2,3,5-trithiacylopentane. These were recrystallized from benzene to a constant melting point of 141–143°C. The yields varied from 25–60 percent.

The selenium analogue was prepared in a similar manner except that it was possible to obtain considerable amounts of 1,4-diphenyl-1,4-diarsa-2,3,5-triselenacyclopentane by extraction with hot benzene of the red precipitate formed during the passage of H_2Se through the alcohol solution.

Crystal Structure Determination

Experimental. The crystal was sealed in a glass capillary, and x-ray data was collected by the Molecular Structure Corporation, College Station, Texas, U.S.A.

Crystal Data. $C_{12}H_{10}As_2Se_3$, $M = 540.9$, $F(000) = 1000$, monoclinic, $a = 16.318(5)$, $b = 7.360(2)$, $c = 12.685(4)$ Å, $\beta = 108.40(2)°$, $V = 1445.6(8)$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centered reflections, $3° < \theta < 17°$, $t = 23(1)°C$, $\lambda = 0.71073$ Å), space group C2/c (No. 15), $Z = 4$, $D_x = 2.49$ g/cm^3. Yellow plate, $0.10 \times 0.10 \times 0.05$ mm, μ (MoK_α) = 129.7 cm^{-1}.

Data collection and processing. CAD4 diffractometer $\omega/2\theta$ mode with scan width, $\Delta\omega = 0.7 + 0.35 \tan\theta$, ω scan speed 2.0–20.0 deg/min, graphite-monochromated MoKα radiation; 1745 symmetry allowed reflections were examined ($\theta \leq 28°$, $0 \leq h \leq 21$, $0 \leq k \leq 9$, $-16 \leq l \leq 15$), of which the intensities of 1339 were measured [$I > 0.5\sigma$ (I), estimated from rapid scans] and 1131 retained for refinement [$|F_0| > 1.0\sigma$ (F_0)]. No significant decay of check reflections was observed. Empirical absorption corrections were applied using Ψ-scan data (max, min relative transmission factors 1.00, 0.80).

Structure analysis and refinement. Trial coordinates for non-hydrogen atoms were taken from those of the isomorphous sulfur compound[17] and the initial least-squares refinement was done isotropically. Next, H-atoms were placed 1.08 Å from appropriate C-atoms and assigned C-atom temperature

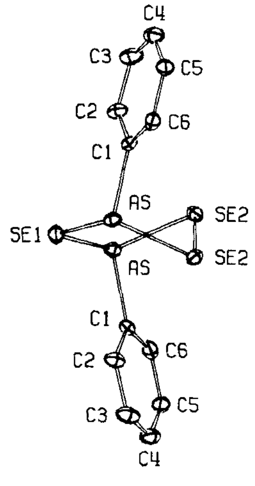


FIGURE 1 ORTEP plot of $Ph_2As_2Se_3$.

TABLE II

Fractional atomic coordinates and equivalent isotropic temperature factors (Å).

	X	Y	Z	U
Se(1)	0.0000(1)	0.3210(2)	0.2500	0.0438(1)
Se(2)	−0.0151(1)	−0.1493(1)	0.3340(1)	0.0381(0)
AS	0.0552(1)	0.1282(1)	0.4083(1)	0.0356(0)
C(1)	0.1724(5)	0.0757(11)	0.4054(7)	0.0340(3)
C(2)	0.2035(6)	0.1175(14)	0.3196(7)	0.0458(4)
C(3)	0.2897(7)	0.0716(16)	0.3293(8)	0.0597(4)
C(4)	0.3421(6)	−0.0047(15)	0.4255(10)	0.0605(5)
C(5)	0.3108(6)	−0.0415(14)	0.5112(10)	0.0584(4)
C(6)	0.2263(6)	−0.0020(12)	0.5028(8)	0.0485(4)
H(2)	0.1637	0.1876	0.2442	0.047
H(3)	0.3149	0.0949	0.2606	0.059
H(4)	0.4091	−0.0346	0.4338	0.061
H(5)	0.3529	−0.1038	0.5859	0.053
H(6)	0.2020	−0.0276	0.5711	0.048

Intramolecular bond distances (Å) and angles (°)

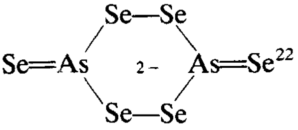
As—Se(1)	2.390(1)	As—Se(2)	2.386(1)
Se(1)—Se(2′)	2.334(1)	As—C(1)	1.962(9)
C(1)—C(2)	1.374(14)	C(1)—C(6)	1.393(11)
C(2)—C(3)	1.414(14)	C(5)—C(6)	1.381(14)
C(3)—C(4)	1.371(14)	C(4)—C(5)	1.366(18)

Se(1)—As—Se(2)	99.76(4)		
As—Se(1)—As′	107.20(6)	As—Se(2)—Se(2′)	98.45(5)
Se(1)—As—C(1)	102.3(2)	Se(2)—As—C(1)	100.0(2)
As—C(1)—C(2)	125.2(6)	As—C(1)—C(6)	114.3(7)
C(2)—C(1)—C(6)	120.5(8)	C(3)—C(4)—C(5)	120.3(10)
C(1)—C(2)—C(3)	118.9(8)	C(1)—C(6)—C(5)	119.4(10)
C(2)—C(3)—C(4)	120.0(11)	C(4)—C(5)—C(6)	120.8(9)

factors. With these parameters held fixed, full-matrix anisotropic refinement of non-H atoms (in two blocks) followed until all shifts were less than 0.06 of the esd's: $R = 0.053$, $R_2 = 0.045$, and goodness of fit, $s = 1.13$. The function minimized was $\sum W(|F_0| - |F_c|)^2$, where $W = 1/\sigma^2(F_0)$ and $\sigma^2(I) = \sigma_0^2(I) + (0.05\,I)^2$, with $\sigma_0(I)$ estimated from counting statistics. A final difference electron map gave max, min of 0.84, $-1.21e/\text{Å}^3$. Local programs and SHELX76[18] were used, with scattering factors taken from the same sources given in an earlier publication.[18]

Note. Atomic coordinates, anisotropic thermal parameters, and useful planes and intermolecular contact distances are deposited with the Cambridge Crystallographic Data Center (CCDC) U.K.

Discussion. An ORTEP drawing is shown in Figure 1. The phenyl group appears normal and As—C(1) = 1.962(9) Å, compared to the sum of single bond covalent radii, 1.21 + 0.77 = 1.98 Å[19] (all covalent and van der Waal's radii will be taken from Reference 19 unless otherwise noted). The experimental distance is slightly longer than that adopted by Domenicano, Vaciago and Coulson,[20] 1.948(5) Å, and the α-angle of the phenyl ring, C(2)-C(1)-C(6) = 120.5(8)°, is also larger than their value, 118.8(3)°. Some of the small discrepancies in bond lengths may be due to the radius of sp^2 carbon being only 0.74 Å.[21] In the (Se—As—Se—As—Se) ring, the distances Se(2)-Se(2)′ = 2.334(1) and As—Se(average = 2.388(2) Å compare well with the sums of covalent radii, 2.34 and 2.38 Å, respectively. There seem to be few structural studies which exhibit As—Se bonds for comparison. In the centrosymmetric anion,



Se—Se = 2.345(2) Å, but the As—Se bond lengths are 2.414(2) (average) and 2.276(2) Å, longer than normal single and double bonds. The lengthening may be associated with the ion's charge. In an adamantane analogue, $C_5H_9As_3$ Se_2[23], four As—Se bonds range from 2.357(3) to 2.369(4) Å, but the As—As bond in the ring (As—Se—As—Se—As) is long, 2.483(3) Å, and the molecule is strained, with As—As—C angles close to 90°. In another strained molecule, $C_{12}H_8As_2Se$,[24] As—Se(average = 2.394(7) Å, with As—Se—As = 86.2(2)°. One aspect of the stereochemistry that seems unusual is the difference in the external phenyl-ring angles, As—C(1)—C(2) = 125.2(6) and As—C(1)—C(6) = 114.3(7)°. Corresponding to these values are short intramolecular contact distances, H(2) . . . Se(1) = 2.87 and H(6) . . . As = 2.86 Å. Similar packing has been observed in the isomorphous compound, $C_{12}H_{10}As_2S_3$[17], where As—C(1)—C(2) = 124.8, and As—C(1)—C(6) = 115(1)°. Intermolecular contact distances in the present structure appear to be normal.

^{77}Se n.m.r. spectrum. Measurement of the ^{77}Se n.m.r. spectrum of 1,4-diphenyl-1,4-diarsa-2,3,5-triselenacyclopentane showed resonances at 705 ppm (As—Se—As) and at 522 ppm (As—Se—Se—As). Measurements were made in $CDCl_3$ and are downfield relative to dimethylselenium as the standard.

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