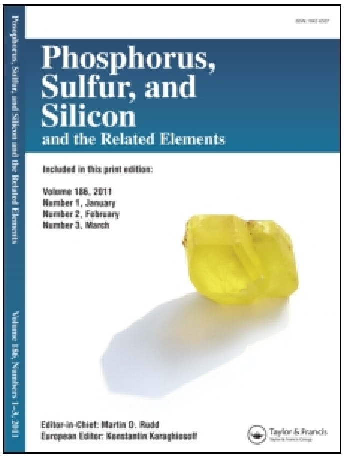

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THE CRYSTAL STRUCTURES OF 10,10'-*BIS*(PHENOXARSINE) OXIDE AND SELENIDE

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THE CRYSTAL STRUCTURES OF 10,10′-*BIS*(PHENOXARSINE) OXIDE AND SELENIDE

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The reaction between 10,10′-*bis*(phenoxarsine) oxide (**I**) and HI gives 10-iodophenoxarsine. The latter, on treatment with H_2Se give 10,10′-*bis*(phenoxarsine) selenide (**II**). The crystal structures of **I** and **II** have been determined from single crystal X-ray data. The unit cell for **I** is monoclinic, $P2_1/c$ (No. 14) with $a = 15.976(3)$ Å, $b = 10.582(2)$ Å, $c = 12.581(2)$ Å, $\beta = 111.70(1)°$; $V = 2018.6$ Å^3; d(calc.) = 1.65 Mg/m^3 at 23°C for four molecules per unit cell. From 3279 reflections for which $I > 0.5\sigma(I)$, $F > \sigma(F)$, $R = 0.041$ with anisotropic thermal parameters for all non-hydrogen atoms and with fixed positions and thermal parameters for hydrogens. One of the phenoxarsina rings deviates from planarity by approximately 5° while the other deviates by more than 24°. The (As—O) distances are 1.810(3) and 1.821(3) Å for the flat and bent ring and the (As—O—As) angle is 122.3(1)°. The bond distances to As and O from C are nearly the same for both rings, but the bond angles with As and the ring O as the apex are systematically larger for the flat ring. For **II** the unit cell is triclinic, $P\bar{1}$ (No. 2) with $a = 9.368(1)$ Å, $b = 14.089$ Å, $c = 9.269(2)$ Å, $\alpha = 111.37(2)$, $\beta = 113.11(2)$, $\gamma = 74.76(1)$; $V = 1037.5$ Å^3, d(calc.) = 1.81 Mg/m^3 for two molecules per unit cell at 23°C. From 2945 reflections for which $I > 0.5\sigma(I)$, $F > \sigma(F)$, $R = 0.055$ with anisotropic thermal parameters for all non-hydrogen atoms and with fixed positions and thermal parameters for hydrogen. One of the phenoxarsina rings deviates by 3° from planarity and the other by 8°. The (As—Se) bond distances are 2.416(1) and 2.406(1) Å. The (As—Se—As) bond angle is 96.66(4)° and the corresponding (As—C) and (C—C) distances in the two rings are nearly the same. In comparison with **I**, the angles with As or O as the central atoms are about the same in both rings of **II**.

INTRODUCTION

We have been involved in the synthesis and structural studies of compounds containing arsenic-chalcogen bonds for a number of years. Structural studies on As—Se bonded derivatives are of special interest because this bond is usually unstable and a relatively small number of crystalline derivatives which contain it have been synthesized. In this paper the synthesis of 10,10′-*bis*(phenoxarsine) selenide is described and its structure is reported. Grindstaff,[1] *et al.*, described the structure of 10,10′-*bis*(phenoxarsine) sulfide and made the unexpected discovery that the phenoxarsine rings are planar. Because of this observation and the availability of 10,10′-*bis*(phenoxarsine) oxide, the structure of this compound has also been determined. The observed variations in the planarities of the phenoxarsine portions of these molecules and additional data on As—X (X = O, S, Se) bond distances are reported in this study.

EXPERIMENTAL SECTION

10,10′-*bis*(phenoxarsine) oxide (**I**) was available as a gift from the Ventron Corp., Beverly, Mass. It was recrystallized from benzene to a constant m.p. of 184–186°. Crystals of good quality were prepared from solutions of the compound in this solvent.

10-Iodophenoxarsine (**III**) was prepared from 5 g (9.96×10^{-3} moles) of **I** dissolved in 150 ml of benzene to which was added 5 ml of conc. HI. The mixture was stirred for 2 h and concentrated at reduced pressure. Overnight cooling resulted in the separation of small, yellow crystals. These were recrystallized from hot ethanol to a constant m.p. of 146–148°C. The literature m.p. for this compound[2] is 144°. 10,10′*bis*(phenoxarsine) selenide (**II**) was prepared under a nitrogen atmosphere from one g of **III** (2.7×10^{-3} moles) dissolved in 200 ml of ethanol containing three ml of pyridine. The mixture was warmed to dissolve the solid and a stream of H_2Se (from $Al_2Se_3 + HCl$) was passed through the stirred solution for two h. On cooling, dark colored crystals formed which were separated by filtration. The foregoing procedure was easily reproducible and the dark needles, m.p. 136–139°C were identified as 10,10′-*bis*(phenoxarsine) selenide: anal.; calcd. (found): %C, 51.00 (50.73); %H, 2.85 (2.87); high resolution mass spec., calcd. (found): 565.87483 (565.87747). Attempts to recrystallize **II** were unsuccessful. Invariably, such attempts resulted in a rapid deposition of elemental selenium. Because of the instability of the crystals their color could not be definitely ascertained, but their dark appearance is due at least in part, to the deposition of elemental selenium. The crystals which separated from the initial reaction mixture were found to be of good quality for X-ray data collection.

Mass spectral behavior of **II**. The molecular ion, M^+, was easily observed. Loss of selenium gives $(M—Se)^+$ at 486. Rupture of the As—Se bond results in the separation of one of the aromatic rings and the resulting fragments, *viz.*, $C_{12}H_8OAsSe^+$ at 323 and $C_{12}H_8OAs^+$ at 243 are present as intense peaks. Loss of arsenic from $(M—Se)^+$ and ring closure gives rise to a strong dibenzofuran peak at 168. Other strong, but unassigned peaks were observed at 139, 125 and 101.

Infrared spectra. Spectra were recorded on the Perkin-Elmer 508B. All three derivatives, including 10,10′-*bis*(phenoxarsine) sulfide which was prepared according to Lewis, Lowry, and Bergeim[3] give very rich spectra. Only results in two regions are reported, those in the region of ν(As—X) and those in the region of ν(C—O—C). The latter are included because of the observed differences in the degrees of non-planarity exhibited among the three compounds.

The assignment of ν(As—X) can be made with a reasonable degree of certainty because all of these vibrations were quite strong. They were in the region expected for a single, covalent bond[4] for the compound under study, but systematically absent in those of the other three (the fourth compound included in this group was 10-iodophenoxarsine). Thus, ν(As—O) was observed at 721 and 683 cm.$^{-1}$, ν(As—S) at 364 and 343 cm.$^{-1}$ and ν(As—Se) at 282 and 240 cm.$^{-1}$. The pairs of bands are probably the result of asymmetric and symmetric modes. For "pure", isolated As—X vibrations, the calculated frequencies[4] are 776, 372, and 277 cm.$^{-1}$ for X = 0, S, and Se, resp.

In the region of C—O—C stretching vibrations the spectra of all four compounds were very similar. For the iodide, bands were present at 1223, 1262 and 1061 cm.$^{-1}$; for the oxide, at 1220, 1255 and a doublet at 1062, 1071 cm.$^{-1}$; for the sulfide at 1233, 1269 and 1050 cm.$^{-1}$ and for the selenide at 1223, 1260 and 1060 cm.$^{-1}$. All of these bands were moderate to strong in intensity. The oxide displayed an intense absorption at 1029 cm.$^{-1}$ and the others a weak absorption at 1023 cm.$^{-1}$.

Crystal structure determination. *Bis*(phenoxarsine) oxide (**I**), $C_{24}H_{16}As_2O_3$, $M_R = 502.0$. X-ray data were collected by the Molecular Structure Corp., College Station, Texas, from a single crystal in the form of a colorless plate $(0.10 \times 0.30 \times 0.40)$ mm^3 mounted on a glass fiber. An Enraf Nonius CAD4 diffractometer was used with graphite monochromatized MoKα radiation, 0.71073 Å. The unit cell is monoclinic, $P2_1/c$, No. 14, with $a = 15.976(3)$, $b = 10.582(2)$, $c = 12.851(2)$ Å, $\beta = 111.70(1)°$, determined from measurements of 2θ for 24 reflections, at 23°C; $V_c = 2018.6$ Å^3; d(X-ray) = 1.65 Mg/m^3 for $Z = 4$; $\mu = 3.32$ mm^{-1}. Intensity data were obtained from $(\theta - 2\theta)$ scans, $2\theta(\text{max.}) = 54°$; $\sigma(I)^2 = \sigma_c^2 + (0.051)^2$ where σ_c^2 was estimated from counting statistics. Lorentz and polarization factors were applied to the data, as well as an empirical absorption correction (relative transmission, T: $0.524 < T < 0.999$; average value = 0.899). Periodic measurements of three standard reflections showed no appreciable changes in their intensities.

Bis(phenoxarsine) selenide (**II**), $C_{24}H_{16}As_2O_2Se$, $M_R = 565.2$. X-ray data were collected in a manner similar to that described for **I**. The crystal was in the form of a tan plate $(0.07 \times 0.20 \times 0.30)$ mm^3. The unit cell is triclinic, $P\bar{1}$, No. 2, $a = 9.3681(1)$, $b = 14.089(2)$, $c = 9.269(2)$ Å, $\alpha = 111.37(2)$, $\beta = 113.11(2)$, $\gamma = 74.61(1)°$. From 2θ values for 25 reflections; $V_c = 1037.5$ A^3; d(X-ray) = 1.81 Mg/m^3; $Z = 2$; $\mu = 4.97$ mm^{-1}; $2\theta(\text{max.}) = 55°$; 4741 unique reflections of which 1233 had $I < 0.5\sigma(I)$; empirical absorption correction, $0.520 < T < 1.000$, average = 0.886.

Structure determination and refinement. (**I**) Of 4647 reflections examined, 250 were discarded as systematically absent, 820 were not measured since preliminary scans indicated that $I < 0.5\sigma(I)$, and 298 reflections were excluded because $F < \sigma(F)$, leaving 3279 reflections used for refinement. A Patterson map yielded coordinates of the As atoms. Three cycles of least squares refinement with isotropic temperature factors followed ($R = 0.32$). An unweighted difference Fourier showed 27 significant peaks of which the three largest were O atoms and the other 24, C atoms. The atomic parameters were refined for a few cycles using isotropic temperature factors. H atoms were then placed 1.08 Å from appropriate C atoms, assigned the same temperature factors as those of the appropriate C atoms and their parameters were kept fixed at these values. A least squares refinement with As, O and C atoms anisotropic was continued until the maximum shift in any parameter was less than 0.10 of its standard deviation: $R = \Sigma \| F_0| - |F_c\| / \Sigma |F_0| = 0.041$; $RW = [\Sigma\omega(|F_0| - |F_c|)^2 / \Sigma\omega / |F_0|^2]^{1/2} = 0.048$ where $\omega = 1/\sigma^2(I) = \sigma c^2 + (0.051)^2$; for 3279 data and 262 parameters, the goodness of fit, $s = 1.27$. The maximum and minimum values in a final difference electron density map are 0.39 and $-0.33e/\text{Å}^3$. SHELX 76[5] modified for a PDP 1144 computer was used for the structure determination.

For compound **II**, 4741 reflections were examined; 1233 had $I < 0.5\sigma(I)$, 563 had $F < \sigma(F)$ and after discarding these, 2945 remained. The structure determination was carried out in the manner described above. The last maximum shift was less than 0.08 of the corresponding standard deviation: $R = 0.055$, $RW = 0.049$, and $s = 1.13$. The maximum and minimum difference densities are 0.53 and $-0.55e/\text{A}^3$.†

DISCUSSION

The crystal coordinates and equivalent isotropic mean square displacements for the non-hydrogen atoms are given in Table I, the intramolecular bond distances and angles in Table II, and the angles between various planes in Table III.

TABLE I

Coordinates and equivalent isotropic temperature factors (Å^2)

$U = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\mathbf{a}_i, \mathbf{a}_j)$

(I) $C_{24}H_{16}As_2O_3$	x/a	y/b	z/c	U
As1	0.41345 (3)	0.03146 (3)	0.26740 (3)	0.04373
As2	0.20589 (3)	−0.04281 (4)	0.17882 (3)	0.04934
01	0.34531 (20)	0.04552 (27)	0.48065 (22)	0.06591
02	0.12881 (19)	−0.09897 (26)	−0.08831 (20)	0.06383
03	0.30974 (16)	−0.01291 (24)	0.15529 (19)	0.04927
C1	0.36832 (28)	0.28825 (39)	0.28814 (32)	0.05933
C2	0.33731 (32)	0.39209 (42)	0.32842 (39)	0.07284
C3	0.30937 (31)	0.37731 (48)	0.41693 (44)	0.07483
C4	0.31109 (27)	0.26032 (51)	0.46384 (34)	0.07158
C5	0.37531 (28)	−0.16451 (49)	0.53279 (34)	0.07258
C6	0.40538 (31)	−0.28290 (47)	0.52117 (40)	0.07712
C7	0.44086 (31)	−0.30742 (42)	0.43971 (40)	0.07520
C8	0.44364 (27)	−0.21224 (38)	0.36891 (33)	0.05750
C9	0.37121 (23)	0.16850 (35)	0.33376 (27)	0.04682
C10	0.34364 (25)	0.15586 (38)	0.42337 (30)	0.05327
C11	0.37885 (24)	−0.06783 (39)	0.46099 (30)	0.05352
C12	0.41230 (24)	−0.09041 (36)	0.37742 (29)	0.04816
C13	0.10462 (28)	0.17785 (43)	0.07364 (41)	0.07071
C14	0.05713 (32)	0.25679 (46)	−0.01601 (53)	0.08289
C15	0.03867 (32)	0.21635 (47)	−0.12260 (51)	0.08541
C16	0.06285 (30)	0.09666 (44)	−0.14543 (38)	0.07445
C17	0.13470 (28)	−0.31718 (41)	−0.07675 (34)	0.06380
C18	0.14835 (31)	−0.42842 (41)	−0.01891 (43)	0.06988
C19	0.17441 (31)	−0.42799 (39)	0.09676 (43)	0.07041
C20	0.19034 (28)	−0.31500 (40)	0.15364 (34)	0.06111
C21	0.13098 (26)	0.05674 (35)	0.05303 (33)	0.05234
C22	0.10841 (26)	0.01738 (37)	−0.05644 (35)	0.05511
C23	0.14784 (25)	−0.20331 (35)	−0.01895 (30)	0.04908
C24	0.17730 (24)	−0.19950 (33)	0.09608 (29)	0.04669

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† Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Requests should be accompanied by the full literature citation for this paper.

TABLE I (*contd*)

(II) $C_{24}H_{16}As_2O_2Se$

	x/*a*	*y*/*b*	*z*/*c*	*U*
Se	0.20267 (9)	0.32423 (5)	0.15914 (8)	0.05460
As1	0.24410 (8)	0.44659 (5)	0.05729 (8)	0.04851
As2	0.39811 (8)	0.18753 (5)	0.07867 (7)	0.04590
01	0.51985 (46)	0.31952 (31)	−0.10920 (45)	0.04981
02	0.44901 (57)	−0.00306 (32)	0.22944 (50)	0.06510
C1	0.54263 (96)	0.49424 (50)	0.30672 (80)	0.06232
C2	0.70307 (102)	0.48886 (54)	0.37437 (81)	0.06504
C3	0.79716 (90)	0.42891 (57)	0.28078 (90)	0.06753
C4	0.72891 (76)	0.37497 (47)	0.11988 (77)	0.05334
C5	0.35252 (74)	0.25086 (46)	−0.36776 (68)	0.04942
C6	0.20580 (83)	0.23801 (51)	−0.48175 (72)	0.05767
C7	0.07131 (78)	0.28684 (57)	−0.43805 (78)	0.06175
C8	0.08829 (75)	0.34602 (51)	−0.27943 (80)	0.05656
C9	0.47037 (72)	0.43575 (41)	0.14235 (67)	0.04422
C10	0.56844 (74)	0.37701 (43)	0.05157 (70)	0.04684
C11	0.36641 (66)	0.31266 (41)	−0.20667 (64)	0.03889
C12	0.23566 (64)	0.36000 (42)	−0.16140 (65)	0.03970
C13	0.61970 (84)	0.23796 (51)	0.40513 (84)	0.06041
C14	0.72438 (85)	0.22324 (63)	0.55190 (90)	0.07147
C15	0.73511 (78)	0.13228 (61)	0.58431 (85)	0.06553
C16	0.64321 (81)	0.05908 (50)	0.47236 (76)	0.05868
C17	0.25083 (86)	−0.08764 (48)	0.01998 (84)	0.05984
C18	0.13032 (89)	−0.09989 (57)	−0.12826 (94)	0.07116
C19	0.08750 (92)	−0.02835 (61)	−0.21374 (92)	0.07896
C20	0.16655 (82)	0.05548 (55)	−0.14753 (83)	0.06317
C21	0.52599 (69)	0.16416 (45)	0.28794 (69)	0.04474
C22	0.53745 (72)	0.07572 (45)	0.32461 (69)	0.04754
C23	0.32848 (75)	−0.00233 (45)	0.08274 (69)	0.04880
C24	0.28671 (72)	0.07166 (41)	0.00254 (69)	0.04527

TABLE II

Bond distances (Å) and bond angles (°)

(I) $C_{24}H_{16}As_2O_3$

As1–O3	1.810 [2]	As2–O3	1.821 [3]
As1–C9	1.926 [4]	As1–C12	1.919 [4]
As2–C21	1.930 [4]	As2–C24	1.931 [3]
O1–C10	1.375 [5]	O1–C11	1.375 [5]
O2–C22	1.374 [5]	O2–C23	1.380 [5]
C9–C10	1.383 [6]	C11–C12	1.386 [6]
C21–C22	1.381 [6]	C23–C24	1.376 [5]
C9–C1	1.390 [6]	C12–C8	1.402 [6]
C21–C13	1.404 [6]	C24–C20	1.404 [6]
C10–C4	1.401 [7]	C11–C5	1.393 [6]
C22–C16	1.388 [6]	C23–C17	1.390 [6]
C4–C3	1.373 [7]	C5–C6	1.370 [7]
C16–C15	1.387 [7]	C17–C18	1.366 [6]
C3–C2	1.376 [8]	C6–C7	1.387 [8]
C14–C15	1.359 [9]	C18–C19	1.388 [8]
C2–C1	1.382 [7]	C7–C8	1.369 [7]
C14–C13	1.398 [7]	C19–C20	1.375 [6]
As1–O3–As2	122.3 [1]		
O3–As1–C9	100.4 [1]	O3–As2–C21	95.0 [2]
O3–As1–C12	99.0 [1]	O3–As2–C24	95.9 [2]
C9–As1–C12	94.6 [2]	C21–As2–C24	93.5 [1]
C10–O1–C11	125.0 [4]	C22–O2–C23	123.0 [3]
As1–C9–C10	124.6 [3]	As2–C21–C22	122.4 [3]
As1–C12–C11	124.5 [3]	As2–C24–C23	122.3 [3]

TABLE II (*contd*)

O1–C10–C9	125.4 [4]	O2–C22–C21	124.9 [3]
O1–C11–C12	125.5 [4]	O2–C23–C24	125.2 [3]
As1–C9–C1	117.5 [3]	As2–C21–C13	118.5 [3]
As1–C12–C8	117.4 [3]	As2–C24–C20	119.9 [3]
O1–C10–C4	114.1 [4]	O2–C22–C16	113.9 [4]
O1–C11–C5	113.9 [4]	O2–C23–C17	113.2 [3]
C9–C1–C2	121.8 [4]	C21–C13–C14	119.9 [5]
C12–C8–C7	121.6 [5]	C24–C20–C19	121.0 [4]
C1–C2–C3	119.3 [4]	C13–C14–C15	119.5 [5]
C8–C7–C6	119.1 [4]	C20–C19–C18	119.7 [4]
C2–C3–C4	120.4 [5]	C14–C15–C16	121.8 [5]
C7–C6–C5	120.7 [5]	C19–C18–C17	120.3 [4]
C3–C4–C10	119.9 [5]	C15–C16–C22	118.7 [5]
C6–C5–C11	119.9 [5]	C18–C17–C23	119.6 [4]
C4–C10–C9	120.6 [4]	C16–C22–C21	121.1 [4]
C5–C11–C12	120.6 [4]	C17–C23–C24	121.6 [3]
C10–C9–C1	117.9 [4]	C22–C21–C13	118.9 [4]
C11–C12–C8	118.0 [4]	C23–C24–C20	117.8 [3]

(II) $C_{24}H_{16}As_2O_2Se$

As1–Se	2.416 [1]	As2–Se	2.406 [1]
As1–C9	1.935 [6]	As1–C12	1.930 [5]
As2–C21	1.934 [5]	As2–C24	1.931 [7]
O1–C10	1.366 [6]	O1–C11	1.372 [6]
O2–C22	1.376 [8]	O2–C23	1.387 [7]
C9–C10	1.392 [9]	C11–C12	1.375 [9]
C21–C22	1.375 [10]	C23–C24	1.384 [10]
C9–C1	1.424 [7]	C12–C8	1.394 [8]
C21–C13	1.393 [8]	C24–C20	1.389 [8]
C10–C4	1.380 [9]	C11–C5	1.401 [7]
C22–C16	1.400 [8]	C23–C17	1.389 [10]
C4–C3	1.375 [8]	C5–C6	1.375 [8]
C16–C15	1.366 [9]	C17–C18	1.380 [9]
C3–C2	1.385 [12]	C6–C7	1.402 [11]
C14–C15	1.390 [14]	C18–C19	1.387 [13]
C2–C1	1.376 [12]	C7–C8	1.369 [9]
C14–C13	1.381 [10]	C19–C20	1.377 [12]

As1–Se–As2	96.66 [4]		
Se–As1–C9	100.8 [2]	Se–As2–C21	100.5 [2]
Se–As1–C12	99.3 [2]	Se–As2–C24	99.5 [2]
C9–As1–C12	94.7 [2]	C21–As2–C24	94.8 [3]
C10–O1–C1	125.0 [6]	C22–O2–C23	124.2 [5]
As1–C9–C10	124.3 [4]	As2–C21–C22	123.7 [4]
As1–C12–C11	123.6 [4]	As2–C24–C23	123.5 [4]
O1–C10–C9	125.3 [5]	O2–C22–C21	126.3 [5]
O1–C11–C12	126.9 [4]	O2–C23–C24	126.2 [6]
As1–C9–C1	118.5 [5]	As2–C21–C13	118.5 [6]
As1–C12–C8	117.7 [5]	As2–C24–C20	119.1 [6]
O1–C10–C4	113.7 [6]	O2–C22–C16	112.6 [6]
O1–C11–C5	112.1 [5]	O2–C23–C17	111.8 [6]
C9–C1–C2	121.1 [7]	C21–C13–C14	122.1 [8]
C12–C8–C7	121.6 [6]	C24–C20–C19	122.4 [8]
C1–C2–C3	120.2 [6]	C13–C14–C15	118.8 [7]
C8–C7–C6	119.0 [5]	C20–C19–C18	118.8 [6]
C2–C3–C4	119.5 [7]	C14–C15–C16	120.3 [6]
C7–C6–C5	120.5 [5]	C19–C18–C17	120.6 [8]
C3–C4–C10	121.1 [7]	C15–C16–C22	120.0 [7]
C6–C5–C11	119.3 [6]	C18–C17–C23	119.0 [7]
C4–C10–C9	121.0 [5]	C16–C22–C21	121.1 [6]
C5–C11–C12	120.9 [5]	C17–C23–C24	122.0 [5]
C10–C9–C1	117.1 [6]	C22–C21–C13	117.7 [6]
C11–C12–C8	118.7 [5]	C23–C24–C20	117.1 [6]

TABLE III

Best planes (distances in Å) and dihedral angles (°) between them

(I) $C_{24}H_{16}As_2O_3$

No. of plane	Atoms in plane	D (max)'	D'' for atom given
1	AS1, O1, C9, C10	C10:-0.011	
2	AS1, O1, C11, C12	C11:-0.013	
3	AS1, O1, C9-C12	AS1:-0.049	
4	C1-C4, C9, C10	C2:0.010	01:0.053
5	C5-C8, C11, C12	C6:-0.008	AS1:-0.122
6	AS2, 02, C21, C22	C22:0.028	
7	AS2, O2, C23, C24	C23:0.024	
8	AS2, O2, C21-C24	AS2:0.194	
9	C13-C16, C21, C22	C14:-0.012	AS2:0.197
10	C17-C20, C23, C24	C19:-0.018	AS2:0.133
11	AS1, AS2, O3		

Dihedral angles

(1)-(2)	5.85	(4)-(5)	4.00
(6)-(7)	26.42	(9)-(10)	22.39
(3)-(8)	39.42		
(3)-(11)	88.61	(8)-(11)	88.70

D' Maximum deviation of a constituent atom from its best plane.
D'' Deviation of atom given from plane specified.

(II) $C_{24}H_{16}As_2O_2SE$

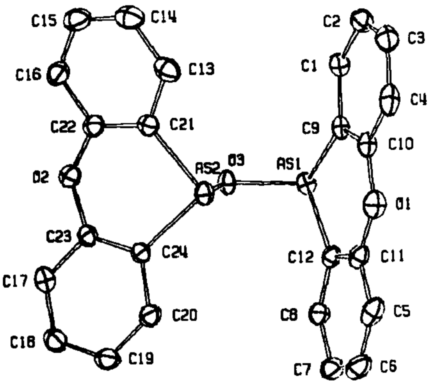
No. of plane	Atoms in plane	D (max)'	D'' for atom given
1	AS1, O1, C9, C10	C10:0.002	
2	AS1, O1, C11, C12	C11:0.005	
3	AS1, O1, C9-C12	AS1:0.015	
4	C1-C4, C9, C10	C1:-0.017	O1:-0.025
5	C5-C8, C11, C12	C7:-0.006	O1:-0.038
6	AS2, O2, C21, C22	C22:0.036	
7	AS2, O2, C23, C24	C23:0.012	
8	AS2, O2, C21-C24	AS2:0.084	
9	C13-C16, C21, C22	C21:0.010	AS2:0.170
10	C17-C20, C23, C24	C24:-0.011	AS2:0.098
11	AS1, AS2, SE		

Dihedral angles

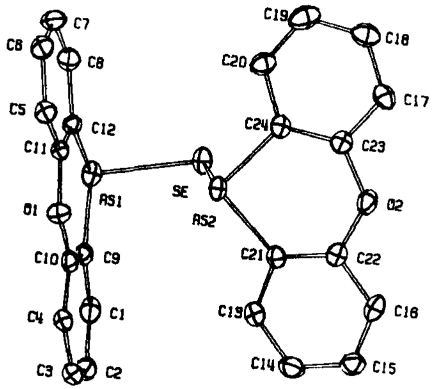
(1)-(2)	1.87	(4)-(5)	3.98
(6)-(7)	9.86	(9)-(10)	6.15
(3)-(8)	90.76		
(3)-(11)	89.27	(8)-(11)	93.87

D' Maximum deviation of a constituent atom from its best plane.
D'' Deviation of atom given from plane specified.

ORTEP drawings of the molecules are given in Figure 1 and packing stereodiagrams in Figure 2. The As—O and As—Se bond distances, 1.81, 1.82 Å and 2.41, 2.42 Å are close to the calculated covalent single bond distances, 1.82 and 2.38 Å resp. That these bonds are uncomplicated single, covalent bonds is reflected also in the locations of the fundamental ν(As—O) and ν(As—Se) stretching vibrations.



(I) $C_{24}H_{16}As_2O_3$.

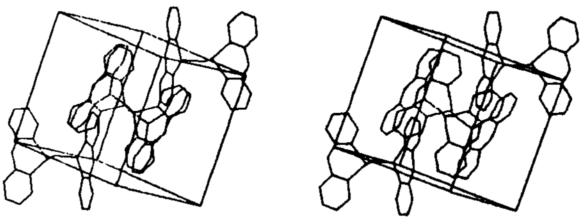


(II) $C_{24}H_{16}As_2O_2Se$.

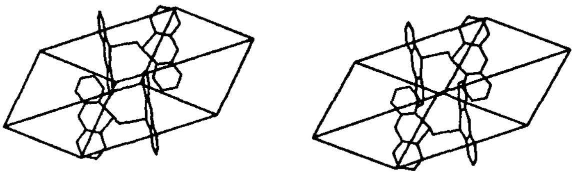
FIGURE 1 ORTEP drawings of (I) $C_{24}H_{16}As_2O_3$ and (II) $C_{24}H_{16}As_2O_2Se$ showing the atom-labeling scheme. H-atoms are omitted. (Johnson, C. K., *ORTEP*, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, 1965.)

The phenyl rings are quite normal, as are the (C—O—C) bond distances and angles. Since relatively few data are available for the bond distances and angles that involve As, some of these will be reviewed. In 1940, Chatt and Mann[6] proposed butterfly shaped structures for 5, 10-disubstituted-5, 10-dihydroarsanthrenes, (IV), assuming an intervalency angle of 97° for As. They synthesized two *p*-tolyl derivatives ($R = p\text{-}CH_3C_6H_4$) and decided from models that these were probably the *cis*-isomer and the *trans*-isomer. In the *cis*-form, both of the *R*-groups lie inside the fold of the ring, while in the *trans*-form, one lies inside the fold and the other, outside.

Jones and Mann[7] reported the preparation of one isomer of the dimethyl compound ($R = CH_3$) and its crystal structure was determined in 1968.[8] It was found to be the butterfly shaped (dihedral angle, DA = 117°) *cis*-isomer. In 1977, Cobbledick, Copes and Einstein[9] determined the structure of the perfluorinated molecule, (V). They found that the molecule was flat (DA = 180°) with one CH_3



(I) $C_{24}H_{16}As_2O_3$.

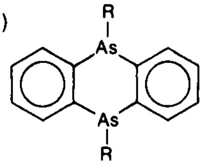


(II) $C_{24}H_{16}As_2O_2Se$.

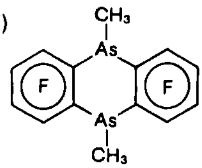
FIGURE 2 Packing stereodiagrams which show the contents of the unit cell of (I) $C_{24}H_{16}As_2O_3$ and (II) $C_{24}H_{16}As_2O_2Se$.

group above the ring and one below (*trans*-form). Prior to these X-ray studies, Mislow, Zimmerman and Melillo[10] had expressed doubts as to whether a stable, sharply bent butterfly structure should be expected for molecules of this general type. They suggested that easy flexing of the central ring should occur and that a planar configuration could not be ruled out by the available experimental evidence.

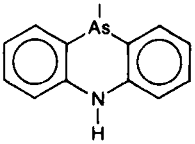
(IV)



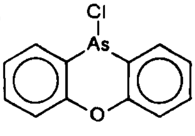
(V)



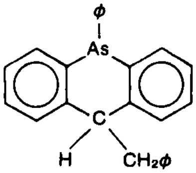
(VI)



(VII)



(VIII)



Cameman and Trotter[11] determined the structure of (**VI**). The ring is folded slightly (DA = 169°) and C1 lies outside of the fold. The position of the H atom attached to N was not reported. Cordes and his coworkers[1,12] determined the structures of the compound (**VII**) and of the sulfur analogue of (**I**) and (**II**), 10,10′-*bis*(phenoxarsine) sulfide. The molecule (**VII**) is folded (DA = 156°) and C1 is outside of the fold. Both parts of 10,10′-*bis*(phenoxarsine) sulfide are nearly flat (DA = 175°, 178°). As part of a series of studies of arsenic heterocycles, Stam[13] determined the structure of (**VIII**), which has DA = 133°.

No obvious relationship between the dihedral angle and other structural parameters of these molecules is apparent to us. The fluorinated molecule, (**V**), has the longest (As—C) bond distances, 1.96(1) and 1.97(1) Å, and the widest (C—As—C) ring angle, 101.2(5)°. In this structure, the (As—CH) distance is very short (1.89 Å) and there is a wide range in both (C—F) (1.33–1.38 Å) and in (C—C) (1.34–1.40 Å) bond distances. For the other molecules mentioned above, the (As—C) distance ranges only from 1.908(9) to 1.953(2) Å, and the (C—As—C) angle from 93.5(1)° to 97.0(4)°, while the dihedral angle ranges drastically from 117° to 178°. [The extreme values of 1.908 Å and 97.0° were found in molecule (**VI**).] The variation in angles (R—As—C) is 95.0(2)° to 100.8(2)°, where R is the substituent on As and C is a ring carbon atom. The great variation in dihedral angles, including the large difference in them found in the two halves of the molecule (**I**) (DA = 156°, 175°) may be due to the effect proposed in Reference (10) from a consideration of the bending and stretching force constants for the molecules that have As in the 9- and 10-positions, namely that easy flexing of the ring system may be anticipated. Thus, the molecules considered here may possess very flat potential surfaces on which large changes in dihedral angle can occur without major alterations in other structural parameters. There are no unusually short intermolecular contact distances in either structure.

No systematic differences are apparent either in the regions of the C—O—C stretching or characteristic aromatic vibrational frequencies of the infrared spectra which reflect differences in ring planarities. This may be due to the great complexity of the spectra, overlapping of bands, or the insensitivity of the method or the instrumentation.

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