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The Molecular Structure of 10-Phenoxarsine Sulfide, an Organoarsenical with Planar Phenoxarsine Moieties

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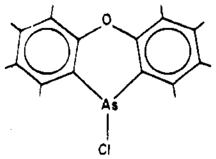
The crystal and molecular structure of 10-phenoxarsine sulfide, $(C_{12}H_8OAs)_2S$, has been determined by single-crystal X-ray diffraction methods. The unit cell is triclinic: $a = 9.033$ (1) Å, $b = 11.435$ (2) Å, $c = 14.114$ (3) Å, $\alpha = 127.83$ (3)°, $\beta = 112.10$ (2)°, and $\gamma = 84.36$ (1)°. The Delauney cell has $a = 9.033$ (1) Å, $b = 11.435$ (2) Å, $c = 13.597$ (3) Å, $\alpha = 124.85$ (3)°, $\beta = 105.89$ (2)°, $\gamma = 95.64$ (1)°, with $d_{\text{measd}} = 1.61$ (1) g cm^{-3} and d_{calcd} (for $Z = 2$) = 1.640 (3) g cm^{-3}. The space group is $P\bar{1}$ (C_i^1; No. 2), and there are two molecules per unit cell. Manual diffractometer methods (Mo radiation, λ 0.71069 Å) were used to obtain 1412 observed ($I \geq 3\sigma(I)$) reflections at 23°. Refinement of the structure by full-matrix least-squares methods, utilizing anisotropic thermal parameters for the As and S atoms and assigned positions and thermal parameters for the H atoms, gave a final R index of 0.033. The molecule has nearly planar phenoxarsine $(C_{12}H_8OAs)$ moieties. The three planes which include all of the atoms of the structure (the two phenoxarsine planes and the As–S–As plane) are very nearly mutually perpendicular. The As–S distances are 2.267 (3) and 2.282 (3) Å, the AsSAs angle is 99.87 (6)°, and all of the bond angles at the arsenic atoms are 94.4–99.8°.

Introduction

The structures of 10-chlorophenoxarsine[1] (**1**) and its antimony pentachloride–oxide adduct,[2] (**2**) showed dihedral angles between the phenyl ring planes of 156.3 and 167.7°, respectively. Interest in the structural effects of the As–S–As coupling on the phenoxarsine units in 10-phenoxarsine sulfide (**3**) and in the possible p → d π bonding in the As–S–As linkage prompted this structural determination. The discovery of planar phenoxarsine fragments in this molecule was completely unexpected.



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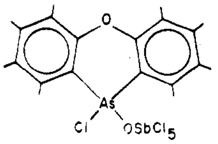

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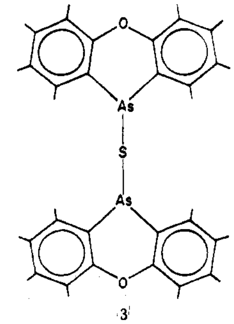

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Experimental Section

10-Phenoxarsine sulfide, $(C_{12}H_8OAs)_2S$, was prepared by the coupling reaction of 10-chlorophenoxarsine with hydrogen sulfide, as described by Lewis, Lowry, and Bergeim.[3] The product of the nearly quantitative reaction was identified by its melting point (161°) and its infrared spectrum. Suitable crystals were obtained by slow cooling of glacial acetic acid solutions. The approximately parallelepiped crystal used for the diffractometer data collection measured 0.11 × 0.11 × 0.20 mm (all ±0.01 mm) in the [100], [010], and [001] directions. The crystal was mounted on a glass fiber with the c axis approximately parallel to the σ axis.

The diffractometer used was a GE XRD-5 manually operated quarter circle system, with Mo Kα (λ 0.71069 Å) radiation filtered with 1-mil zirconium foil. A scintillation counter was used with a pulse height analyzer set for a 90% window. Least-squares refinement[4] of the setting angles of 27 carefully centered reflections gave, at 23°, $a = 9.033$ (1) Å, $b = 11.435$ (2) Å, $c = 14.114$ (3) Å, $\alpha = 127.83$ (3)°, $\beta = 112.10$ (2)°, and $\gamma = 84.36$ (1)°; this unit cell was used for data collection, the solution of the structure, and for this report. The Delauney reduced cell has $a = 9.033$ (1) Å, $b = 11.435$ (2) Å, $c = 13.597$ (3) Å, $\alpha = 124.85$ (3)°, $\beta = 105.89$ (2)°, and $\gamma = 95.64$ (1)°, obtained by $a_2 = a_1$, $b_2 = -b_1$, $c_2 = -a_1 - c_1$. The crystal density, measured by suspension in a mixture of n-butyl bromide and 1,2-dibromo-1,1-dichloroethane, is 1.61 (1) g cm^{-3}, which compares with 1.640 (3) g cm^{-3} calculated for two formula units per unit cell. Space group $P\bar{1}$ imposes no crystallographic symmetry on the molecules of the structure.

Absorption corrections were neglected. Approximation of the crystal shape as cylindrical makes $\mu r_{\max} = 0.39$ and absorption correction factors for I range from 1.95 to 1.93. No corrections were made for extinction.

For intensity data collection a θ–2θ scan of 2.0° in 2θ was made at a speed of 2°/min with a takeoff angle of 3°. Stationary crystal–stationary counter background readings were taken for 10 sec at each end of the scans. All reflections with $0° < 2\theta < 40°$ were examined (3869). Of these, 1412 reflections had $I \geq 3\sigma(I)$; these were used for the solution and refinement of the structure. Four reflections were measured periodically during the 12-day data collection as a monitor of crystal and electronic stability. An abrupt and permanent decrease of 5% in the intensity of all four reflections midway through the data collection was found to have electronic orgins, and a simple correction was made.

The standard deviations for I were calculated by $\sigma(I) = (S + BT^2 + 0.0016\,I^2)^{1/2}$ (where S = total scan count, B = sum of the background counts, T = (scan time)/(total background time), and $I = S - BT$), except for a small number of reflections for which the two background readings differed by more than twice the calculated σ due to tailing of the reflection peak. For the latter reflections the standard deviations were set equal to the deviation of the background readings from the mean background value.

Scattering factors for neutral atoms were calculated from the analytical functions of Cromer and Waber,[5] and real and imaginary anomalous dispersion corrections were made for As and S using the values given by Cromer.[6] All calculations were done with the IBM 360/50 computer at the University of Arkansas Computer Center, using the programs previously described.[1]

Solution and Refinement of the Structure

The structure was solved using visually estimated Weissenberg film data prior to the collection of the diffractometer data used for the refinement. The three heavy atoms were located by analysis of a three-dimensional sharpened Patterson map. The phenyl rings were located by Fourier methods and refined originally as

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[1] J. E. Stuckey, A. W. Cordes, L. B. Handy, R. W. Perry, and C. K. Fair, *Inorg. Chem.*, **11**, 1846 (1972).

[2] R. J. Holliday, R. W. Broach, L. B. Handy, A. W. Cordes, and L. Thomas, *ibid.*, **11**, 1849 (1972).

[3] W. L. Lewis, C. D. Lowry, and F. H. Bergeim, *J. Amer. Chem. Soc.*, **43**, 891 (1921).

[4] A. Foust, Program ANGSET, University of Wisconsin, 1968.

[5] D. T. Cromer and J. T. Waber, Los Alamos Scientific Laboratory, private communications.

[6] D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

TABLE I[a]

FINAL ATOMIC POSITIONAL AND ISOTROPIC THERMAL PARAMETERS FOR $(C_{12}H_8OAs)_2S$

Atom	*X*	*Y*	*Z*	*B*, Å^2
S	0.2530 (3)	0.2944 (2)	0.2014 (2)	
As(1)	0.1172 (1)	0.4455 (1)	0.1593 (1)	
As(2)	0.1353 (1)	0.3077 (1)	0.3245 (1)	
O(1)	0.2628 (7)	0.4800 (7)	−0.0065 (6)	4.9 (1)
O(2)	−0.1222 (6)	0.5415 (6)	0.3461 (5)	3.7 (1)
C(1)	0.0692 (9)	0.3230 (9)	−0.0265 (7)	3.2 (2)
C(2)	−0.0511 (11)	0.1939 (10)	−0.1137 (9)	4.8 (2)
C(3)	−0.0987 (11)	0.0181 (11)	−0.2495 (10)	5.4 (2)
C(4)	−0.0250 (12)	0.1453 (11)	−0.9274 (9)	5.2 (2)
C(5)	0.0929 (11)	0.2675 (11)	−0.2174 (9)	5.0 (2)
C(6)	0.1438 (10)	0.3573 (9)	−0.0785 (8)	3.6 (2)
C(7)	0.2999 (9)	0.5805 (9)	0.2139 (8)	3.3 (2)
C(8)	0.3857 (12)	0.6877 (11)	0.3478 (10)	5.2 (2)
C(9)	0.5120 (13)	0.7941 (12)	0.3925 (10)	6.5 (3)
C(10)	0.5448 (13)	0.7930 (12)	0.3062 (11)	6.7 (3)
C(11)	0.4632 (12)	0.6881 (11)	0.1732 (10)	5.5 (2)
C(12)	0.3389 (10)	0.5792 (9)	0.1284 (8)	3.5 (2)
C(13)	−0.0898 (9)	0.2776 (8)	0.2171 (7)	3.0 (2)
C(14)	−0.1681 (10)	0.1294 (10)	0.1057 (9)	4.2 (2)
C(15)	−0.3304 (11)	0.0993 (10)	0.0265 (9)	4.6 (2)
C(16)	−0.4155 (11)	0.2170 (10)	0.0574 (9)	4.5 (2)
C(17)	−0.3443 (10)	0.3649 (10)	0.1664 (9)	4.2 (2)
C(18)	−0.1778 (9)	0.3922 (9)	0.2446 (8)	3.4 (2)
C(19)	0.1596 (9)	0.5238 (8)	0.4507 (7)	3.1 (2)
C(20)	0.3095 (10)	0.6041 (10)	0.5532 (8)	4.0 (2)
C(21)	0.3382 (11)	0.7594 (11)	0.6429 (9)	5.2 (2)
C(22)	0.2134 (11)	0.8385 (10)	0.6330 (9)	4.8 (2)
C(23)	0.0613 (10)	0.7609 (9)	0.5333 (8)	3.8 (2)
C(24)	0.0373 (9)	0.6037 (9)	0.4419 (7)	3.3 (2)
H(1)	−0.108	0.165	−0.073	5.0
H(2)	−0.192	0.011	−0.316	5.0
H(3)	−0.062	0.203	−0.414	5.0
H(4)	0.149	0.296	−0.258	5.0
H(5)	0.356	0.689	0.417	5.0
H(6)	0.579	0.878	0.495	5.0
H(7)	0.640	0.876	0.34	5.0
H(8)	0.492	0.687	0.104	5.0
H(9)	−0.099	0.038	0.083	5.0
H(10)	−0.390	−0.015	−0.059	5.0
H(11)	−0.543	0.193	−0.005	5.0
H(12)	−0.013	0.457	0.187	5.0
H(13)	0.406	0.543	0.561	5.0
H(14)	0.456	0.820	0.721	5.0
H(15)	0.235	0.961	0.705	5.0
H(16)	−0.036	0.822	0.526	5.0

[a] In all of the tables, unless noted otherwise, the numbers in parentheses are estimated standard deviations in the least significant digit(s) of the preceding parameter.

rigid groups using the film data. When the rigid group constraints were removed and all nonhydrogen atoms were refined (diffractometer data) with isotropic thermal motion R_1 $(=\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ was 0.064.

In the least-squares refinement, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where w is $((I_0 + \sigma(I_0))^{1/2} - F_o)^{-2}$ and the weighted residual R^2 is defined as $(\Sigma w||F_o| - |F_c||^2/\Sigma wF_o^2)^{1/2}$. When the hydrogen atoms were positioned in calculated positions (Table III) and the arsenic and sulfur atoms were refined with anisotropic thermal parameters, R_1 and R_2 became 0.033 and 0.037, respectively. This final refinement consisted of 132 parameters and 1399 reflections; 11 reflections were removed because of obvious reading errors in the manual data collection. In the final cycle of refinement no positional parameter shifted by more than 0.66σ. The standard deviation of an observation of unit weight was 0.88, and no $\Delta F/\sigma$ values were greater than 4.[7] A final difference map did not have any peaks which were interpretable chemically; the highest electron density was 0.35 e/Å^3, which is equal to 7% of the maximum electron density of a carbon atom on a regular electron density map. Inspection of the reflection list of the final least squares did not reveal any $\Delta F/\sigma$ dependence on either F or θ values.

The final positional and isotropic thermal parameters are given in Table I, and Table II gives the final anisotropic thermal parameters.

TABLE II

ANISOTROPIC THERMAL PARAMETERS[a] AND ROOT-MEAN-SQUARE VIBRATION AMPLITUDES OF SULFUR AND ARSENIC IN $(C_{12}H_8OAs)_2S$

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
S	139 (4)	127 (4)	100 (3)	58 (3)	62 (3)	78 (3)
As(1)	112 (2)	113 (2)	89 (1)	39 (1)	51 (1)	68 (1)
As(2)	113 (2)	118 (2)	95 (1)	38 (1)	47 (1)	78 (1)

Rms Amplitudes (Å)

Atom	Minimum	Intermediate	Maximum
S	0.18	0.22	0.24
As(1)	0.18	0.20	0.22
As(2)	0.18	0.21	0.23

[a] The anisotropic temperature factor is in the form of exp $[-(\beta_{11})h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

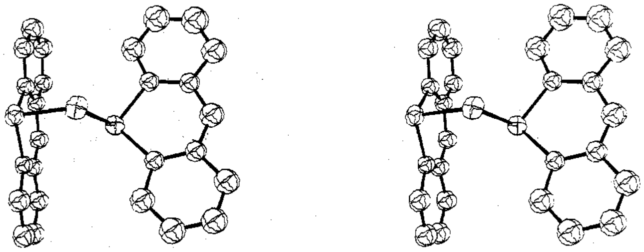

Figure 1.—Stereo ORTEP drawing of the 10-phenoxarsine sulfide molecule. As(1) is on the right, As(2) on the left. The lower right ring is the ring of C(1); the upper right that of C(7); the lower left that of C(13); and the upper left that of C(19).

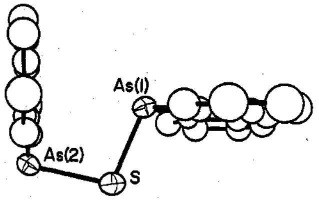

Figure 2.—The "end view" of the 10-phenoxarsine sulfide molecule, showing the relative orientations of the two phenoxarsine rings.

Discussion

Figures 1, 2, and 3 show the molecular and crystal structure of the 10-phenoxarsine sulfide molecule. The intramolecular distances and angles are given on Table III.

The most striking feature of the molecular structure is the near planarity of the $(C_{12}H_8AsO)$ moieties. Table IV shows that one of the three-ring "halves" of the molecule is planar to the extent that the largest displacement of any atom from the least-squares best plane is 0.14 Å (the As atom), and the second largest displacement is 0.084 Å. The other $(C_{12}H_8AsO)$ unit, which contains As(2), is even more nearly planar; the largest deviation from the least-squares best plane is 0.04 Å. If each $(C_{12}H_8AsO)$ fragment is considered to be two (C_6H_4OAs) planar units sharing As and O atoms, the four (C_6H_4OAs) units are planar within 0.02, 0.03, 0.04, and 0.05 Å, and the dihedral angles at the two As···O lines of fold are 175.2° (As(1)–O(1)

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[7] A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1852. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

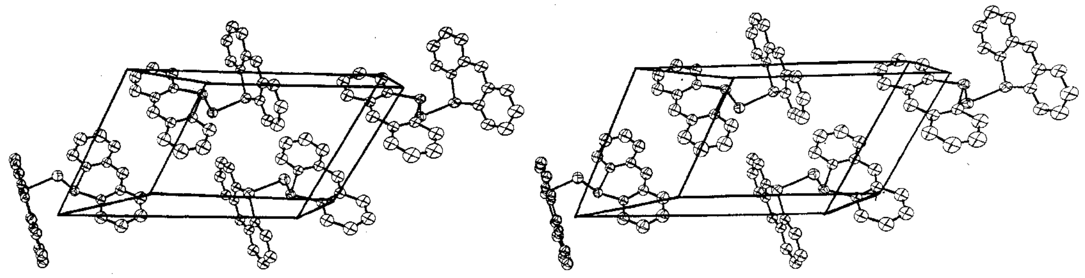

Figure 3.—Stereo ORTEP drawing of 10-phenoxarsine sulfide. The origin of the unit cell shown is the front, lower, right corner. The *b* axis is most nearly perpendicular to the paper, the *a* axis is most nearly vertical, and the *c* axis is horizontal.

TABLE III

SELECTED DISTANCES AND ANGLES IN $(C_{12}H_8OAs)_2S$

Atoms	Dist, Å	Atoms	Angles, deg
As(1)–S	2.267 (3)	As(1)–S–As(2)	99.87 (6)
As(2)–S	2.282 (3)	S–As(1)–C(1)	99.5 (3)
As(1)–C(1)	1.95 (1)	S–As(1)–C(7)	99.8 (3)
As(1)–C(7)	1.95 (1)	S–As(2)–C(13)	99.3 (3)
As(2)–C(13)	1.93 (1)	S–As(2)–C(19)	99.8 (3)
As(2)–C(19)	1.93 (1)	S–As–C (av)	99.6 (2)[a]
As–C (av)	1.94 (1)[a]	As(1)–C(1)–C(6)	124.3 (6)
O(1)–C(6)	1.34 (1)	As(1)–C(7)–C(12)	123.7 (6)
O(1)–C(12)	1.38 (1)	As(2)–C(13)–C(18)	123.9 (7)
O(2)–C(18)	1.36 (1)	As(2)–C(19)–C(24)	123.8 (7)
O(2)–C(24)	1.40 (1)	As–C(av)	123.9 (2)[a]
O–C (av)	1.38 (2)[a]	C(1)–As(1)–C(7)	94.4 (4)
C(1)–C(2)	1.40 (1)	C(13)–As(2)–C(19)	95.2 (4)
C(2)–C(3)	1.41 (2)	C(6)–O(1)–C(12)	125.6 (6)
C(3)–C(4)	1.35 (2)	(C18)–O(2)–C(24)	124.5 (6)
C(4)–C(5)	1.35 (2)	O(1)–C(6)–C(1)	125.0 (6)
C(5)–C(6)	1.43 (2)	O(1)–C(12)–C(7)	126.2 (6)
C(6)–C(1)	1.39 (2)	O(2)–C(18)–C(13)	126.8 (7)
C(7)–C(8)	1.39 (2)	O(2)–C(24)–C(19)	125.8 (5)
C(8)–C(9)	1.40 (2)	O–C–C (av)	126.0 (8)[a]
C(9)–C(10)	1.35 (2)	C(1)–C(2)–C(3)	119.7 (6)
C(10)–C(11)	1.37 (2)	C(2)–C(3)–C(4)	121.2 (11)
C(11)–C(12)	1.41 (1)	C(3)–C(4)–C(5)	121.3 (10)
C(12)–C(7)	1.37 (2)	C(4)–C(5)–C(6)	119.0 (7)
C(13)–C(14)	1.41 (1)	C(5)–C(6)–C(1)	120.9 (8)
C(14)–C(15)	1.38 (1)	C(6)–C(1)–C(2)	117.8 (8)
C(15)–C(16)	1.39 (2)	C(7)–C(8)–C(9)	118.6 (8)
C(16)–C(17)	1.38 (2)	C(8)–C(9)–C(10)	120.1 (9)
C(17)–C(18)	1.42 (1)	C(9)–C(10)–C(11)	123.1 (13)
C(18)–C(13)	1.38 (1)	C(10)–C(11)–C(12)	116.6 (12)
C(19)–C(20)	1.38 (1)	C(11)–C(12)–C(7)	121.5 (10)
C(20)–C(21)	1.38 (2)	C(12)–C(7)–C(8)	120.0 (7)
C(21)–C(22)	1.39 (2)	C(13)–C(14)–C(15)	120.5 (8)
C(22)–C(23)	1.38 (1)	C(14)–C(15)–C(16)	119.4 (6)
C(23)–C(24)	1.40 (1)	C(15)–C(16)–C(17)	122.6 (11)
C(24)–C(19)	1.38 (1)	C(16)–C(17)–C(18)	116.8 (10)
C–C (av)	1.39 (2)[a]	C(17)–C(18)–C(13)	122.1 (10)
C–H (assigned)	1.09	C(18)–C(13)–C(14)	118.6 (7)
		C(19)–C(20)–C(21)	121.5 (10)
		C(20)–C(21)–C(22)	120.0 (7)
		C(21)–C(22)–C(23)	119.7 (7)
		C(22)–C(23)–C(24)	118.9 (6)
		C(23)–C(24)–C(19)	122.0 (10)
		C(24)–C(19)–C(20)	117.8 (8)
		C–C–C (av)	119.7 (18)[a]
		C–C–H (assigned)	120.0

[a] The average values reported are the weighted averages, and the σ's for the average values are the rms deviations from the average.

TABLE IV

ATOMIC DISPLACEMENTS (Å) FROM LEAST SQUARES PLANES IN $(C_{12}H_8OAs)_2S$[a]

Atom	Plane 1	Plane 2	Plane 3	Atom	Plane 4	Plane 5	Plane 6
C(1)	−0.02		0.01	C(13)	0.01		0.02
C(2)	−0.04		−0.06	C(14)	0.02		0.04
C(3)	0.01		−0.05	C(15)	0.00		0.02
C(4)	0.02		−0.03	C(16)	−0.02		−0.02
C(5)	0.02		0.01	C(17)	−0.01		−0.02
C(6)	−0.03		0.01	C(18)	0.00		−0.01
As(1)	0.04	−0.05	0.14	As(2)	−0.02	0.03	−0.01
O(1)	−0.01	0.02	0.08	O(2)	0.01	−0.01	−0.02
C(7)		0.04	−0.01	C(19)		−0.02	−0.04
C(8)		0.03	−0.05	C(20)		−0.03	−0.04
C(9)		0.01	−0.08	C(21)		0.01	0.02
C(10)		−0.04	−0.01	C(22)		0.02	0.04
C(11)		−0.03	0.02	C(23)		0.00	0.01
C(12)		0.03	0.02	C(24)		0.00	−0.01

[a] The least-squares planes were calculated with unit weights for each of the atoms whose distances to the plane are given.

fragment) and 178.5° (As(2)–O(2) fragment). In comparison to the dihedral angles of 156.3° in $C_{12}H_8OAsCl$ (Figure 1), 169.3° in $C_{12}H_8NHAsCl$,[8] and 167.7° in $C_{12}H_8O_2AsCl \cdot SbCl_5$ (Figure 2), it can be seen that the changes toward planarity in the present structure are dramatic.

The arrangement of the near-planar fragments around the sulfur atom is such that one heterocyclic unit lies outside the S–As–S bond angle, and the other lies inside this angle (Figures 2 and 3). The As–S–As plane is very nearly perpendicular to the two heterocycle rings; the plane of the As–S–As linkage forms an 88.2° angle with the heterocyle of As(1) and an 89.9° angle with the heterocycle of As(2). The intersection of the plane of the As(1) heterocycle with the plane of the As(2) heterocycle makes an 86.4° angle. The oxygen atoms O(1) and O(2) are within 0.18 and 0.10 Å of being in the As–S–As plane.

The As–S distances of 2.266 (3) and 2.282 (3) Å are comparable to the values found in the five-membered arsenic–sulfur ring compound $As_2S_3(C_6H_5)_2$ and are equal to, or longer than, the values found for the arsenic–sulfur cage molecules.[9] As–S bonds as short as 2.08 (2) Å[9] have been found for thioarsenates. It would therefore appear that the As–S bond lengths in 10-phenoxarsine sulfide reflect little, if any, multiple bond character in spite of the presence of lone-pair electrons and available d orbitals on all three of the atoms. The As–S–As bond angle of 99.87 (6)° is also in the range expected for a sulfur atom forming two σ bonds.

All three bond angles at both arsenic atoms are within a few degrees of 98°, as was found for the other As heterocyclics of this type mentioned above. The O–C and C–C ring parameters are in good agreement with previously reported values. The packing of the molecule in the triclinic unit cell is shown in Figure 3. No intermolecular contacts were shorter than the corresponding sum of the van der Waals radii.[10]

We find no ready explanation for the difference in the dihedral angles of the planar 10-phenoxarsine sulfide and the folded 10-phenoxarsine chloride. In neither structure does the dihedral angle of the $C_{12}H_8OAs$ group appear to be dictated by unusually sort packing distances. Table V compares the average values for

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[8] A. Camerman and J. Trotter, *J. Chem. Soc.*, 730, (1965).

[9] *Cf.* L. G. McRae, R. W. Perry, C. K. Fair, A. Hunt, and A. W. Cordes, *Inorg. Chem.*, **11**, 618 (1972), and references therein.

[10] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, New York, N. Y., 1960.

TABLE V

CENTRAL RING BOND DISTANCES (Å) AND ANGLES (DEG) (AVERAGE VALUES) OF 10-PHENOXARSINE CHLORIDE AND 10-PHENOXARSINE SULFIDE

	As–C	C–C	C–O	C–As–C	As–C–C	O–C–C	C–O–C
Sulfide	1.94 (1)	1.38 (1)	1.38 (2)	94.8 (4)	123.9 (2)	126.0 (8)	125.0 (5)
Chloride	1.93 (2)	1.38 (1)	1.40 (2)	94.6 (7)	123 (3)	124 (2)	124 (1)

the central-ring bond distances and bond angles. The comparison reveals that the 20° dihedral angle change toward planarity in the sulfide molecule has occurred with only slight changes in the central ring bond distances and angles. Further structural investigations are anticipated in order to elucidate the electronic factors which govern these dihedral angle changes.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CANTERBURY,
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Structural Studies of Derivatives of Methinyltricobalt Enneacarbonyls. VI.[1] Crystal Structure of Phenylmethinyltricobalt Hexacarbonyl–Mesitylene, $(C_6H_5)CCo_3(CO)_6 \cdot \pi\text{-}C_6H_3(CH_3)_3$

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The crystal and molecular structure of $(C_6H_5)CCo_3(CO)_6$–π-mesitylene, a product of the direct reaction of $(C_6H_5)CCo_3(CO)_9$ with mesitylene, has been determined. Crystals are orthorhombic, space group D_{2h}^{16}-*Pnma*, with four molecules in a unit cell of dimensions $a = 19.259$ (3), $b = 13.088$ (2), $c = 8.731$ (1) Å. Molecular symmetry C_s-*m* is required. X-Ray data were collected by counter methods in association with a four-circle diffractometer using Mo Kα radiation. All atoms were treated anisotropically in a full-matrix least-squares refinement to a conventional R factor of 0.057 for the 969 reflections having $|F^2| > \sigma|F^2|$. The molecular structure is derived from the parent $YCCo_3(CO)_9$ structure by replacement of the three CO groups attached to one of the Co atoms of the Co_3 triangle by one molecule of mesitylene. The plane of the mesitylene ring is approximately normal to the line joining the nearest Co atom to the centroid of the tetrahedral Co_3C group. Co–Co bond lengths are in the range 2.441 (2)–2.477 (3) Å and the mean Co–C(mesitylene) length is 2.15 (3) Å.

Introduction

When methinyltricobalt enneacarbonyls of general composition $YCCo_3(CO)_9$ (Y = alkyl or aryl) are heated with various arenes, complexes of composition $YCCo_3(CO)_6 \cdot$arene are obtained.[2] These complexes are distinct from the various linked cluster compounds[1,3–5] which are obtained when Y is Cl or Br. Evidence from nmr and infrared spectra was equivocal on the mode of attachment of the arene molecule, but replacement of the three carbonyl groups of one cobalt atom was indicated. The compound in which Y = phenyl and the arene is mesitylene was selected for detailed structure analysis, a preliminary account of which has been given.[6]

Experimental Section

An analyzed sample of $C_6H_5CCo_3(CO)_6 \cdot$mesitylene was kindly supplied by Dr. B. H. Robinson. The crystals, obtained by fractional sublimation, were large black prisms from which smaller fragments, suitable for X-ray diffraction, had to be cut.

Crystallographic Data.[7]—$Co_3C_{22}O_6H_{17}$, mol wt 553.7, is orthorhombic with $a = 19.259$ (3), $b = 13.088$ (2), $c = 8.731$ (1) Å; $V = 2201$ Å^3; $d_{obsd} = 1.64$ (5) g/cm^3; $Z = 4$; $d_{calcd} = 1.67$ g/cm^3; μ(Mo Kα) = 23.6 cm^{-1}. The two space groups consistent with observed systematic absences of X-ray reflections ((0*kl*) for $k + l$ odd and (*hk*0) for h odd) are C_{2v}^{9}-$Pn2_1a$ and D_{2h}^{16}-*Pnma*. Choice of the centrosymmetric *Pnma* was finally made on the basis of the Patterson function and the successful structure refinement.

Unit cell dimensions and their estimated standard deviations were obtained at room temperature (23 ± 2°) with Mo Kα_1 radiation (λ 0.7093 Å) by least-squares refinement of the setting angles of 12 high-angle reflections for the crystal mounted on a Hilger-Watts four-circle diffractometer. The experimental density was obtained by flotation of crystals in aqueous zinc bromide solution.

The crystal used for all unit cell and intensity measurements was approximately a cube of edge 0.25 mm and its ten faces were identified as (011), $(0\bar{1}\bar{1})$, (201), $(\bar{2}0\bar{1})$, $(12\bar{1})$, $(\bar{1}\bar{2}1)$, and the forms {210}. The procedures for the collection of intensity data from the four-circle diffractometer using a θ–2θ scan technique were essentially as described in detail in part V of this series.[1] The crystal mosaicity was 0.10°. The scan range was 1.28° in 2θ and the reciprocal lattice was explored out to $2\theta = 45°$ beyond which there were very few intensities above background. All independent *hkl* reflections out to this limit were recorded followed by all $\bar{h}\bar{k}\bar{l}$ reflections for which $I(hkl) > \sigma[I(hkl)]$. Absorption corrections were applied using a Gaussian integration method and transmission coefficients were in the

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(1) Part V: M. D. Brice and B. R. Penfold, *Inorg. Chem.*, **11**, 1381 (1972).

(2) B. H. Robinson and J. L. Spencer, *J. Chem. Soc. A*, 2045 (1971).

(3) R. J. Dellaca, B. R. Penfold, B. H. Robinson, W. T. Robinson, and J. L. Spencer, *Inorg. Chem.*, **9**, 2197, 2204 (1970).

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(6) M. D. Brice, R. J. Dellaca, B. R. Penfold, and J. L. Spencer, *Chem. Commun.*, 72 (1971).

(7) Here and throughout this paper, the figures given in parentheses are estimated standard deviations in the least significant digits quoted.