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The Molecular Structure of 10-Phenoxarsine Chloride, $C_{12}H_8OAsCl$

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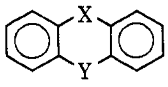
Received December 14, 1971

The crystal and molecular structure of 10-phenoxarsine chloride, $C_{12}H_8OAsCl$, has been determined by single-crystal X-ray diffraction methods. The unit cell is monoclinic: $a = 5.7596$ (6) Å, $b = 14.641$ (2) Å, $c = 13.788$ (1) Å, $\beta = 109.80$ (1)°, $d_{\text{measd}} = 1.71$ (1) g cm^{-3}, and d_{calcd} ($Z = 4$) $= 1.691$ g cm^{-3}. The space group is $P2_1/c$ (C_{3h}^5; No. 14). Manual diffractometer methods (Mo radiation, λ 0.71069 Å) were used to obtain 434 observed ($I \geqslant 2\sigma(I)$) reflections at 23°. Final full-matrix least-squares refinement using anisotropic thermal parameters for As and Cl and assigned positional and thermal parameters for the hydrogen atoms gave an R index of 0.047. The As–Cl bond distance is 2.255 (5) Å, and the average As–C distance is 1.93 (2) Å. All of the bond angles at the arsenic are 94–98°. The two C_6H_4OAs "halves" are planar within 0.04 Å, and the angle of fold at the As···O line is 156.3°. A comparison of these structural parameters with those of phenarsazine chloride suggests a smaller amount of aromatic character in 10-phenoxarsine chloride.

Introduction

In the general class of three-ring molecules illustrated



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in structure **1**, the dihedral angle between the two half-molecule planes which intersect at the X···Y line appears to be a sensitive measure of the extent to which the X and Y atoms participate in delocalized bonding with the phenyl rings. Thus, when X and Y are CH and CH (anthracene),[1] CH and N (acridine),[2] N and N (α-phenazine),[3] or C=O and C=O (anthraquinone)[4] (situations where the central ring is formally unsaturated), the molecule is completely planar (dihedral angle of 180°). When X and Y are NH and S (the phenylthiazines)[5] the dihedral angle is 138–139.4°; S and S (thianthrene)[6] give an angle of 128.1°; S(O) and S(O) (thianthrene dioxide)[7] give 133.6°; and S and O (phenoxthionine)[8] give 138.4°. Several theoretical discussions of the geometry of these molecules are available.[9]

In a study of one of this type of heterocyclic molecule which incorporated the fourth row element As (X = NH, Y = AsCl), Trotter[10] found a dihedral angle of 169.3°, a value which is intermediate to those of the general classes mentioned above. This geometry is close enough to complete molecular planarity to invite speculation on the possible utilization of the d orbitals of the arsenic atom to enhance delocalized bonding in the molecule. In order to pursue the structural evidence of such cyclic p → d π bonding, we report here the structure of 10-phenoxarsine chloride (X = O, Y = AsCl), which is isoelectronic to the molecule studied by Trotter. In succeeding papers we report the structures of the antimony pentachloride adduct of 10-phenoxarsine oxychloride, and 10-phenoxarsine sulfide.

Experimental Section

10-Phenoxarsine chloride was prepared by the reaction of $AsCl_3$ with diphenyl ether, according to the method of Lewis, Lowry, and Bergeim.[11] The compound was identified by its melting point (124°) and its mass spectrum. Suitable crystals were obtained by slow evaporation of a solution of the product in a chloroform–octane mixed solvent. The approximately parallelepiped crystal used for data collection measured 0.30 × 0.31 × 0.45 mm (all ±0.01 mm) in the [01$\bar{1}$], [011], and [100] directions. The crystal was mounted on a glass fiber with the a axis roughly parallel to the ϕ axis.

The diffractometer used was a GE XRD-5 manually operated quarter circle system, with Mo Kα (λ 0.71069 Å) radiation filtered by 1-mil zirconium foil. A scintillation counter was used with a pulse height analyzer set for a 90% window. Least-squares refinement[12] of the setting angles of 21 carefully centered reflections gave, at 23°, $a = 5.7596$ (6) Å, $b = 14.641$ (2) Å, $c = 13.788$ (1) Å, and $\beta = 109.80$ (1)°. The crystal density, measured by suspension in a mixture of ethyl iodide and tetrachloroethylene, is 1.71 (1) g cm^{-3}, which compares with 1.691 g cm^{-3} calculated for four formula units per unit cell. Systematic absences indicated the space group to be $P2_1/c$ (C_{2h}^5; No. 14). Four molecules per unit cell in $P2_1/c$ imposes no crystallographic symmetry on the molecules.

Absorption corrections were made using the program DEAR.[13] The linear absorption coefficient for Mo Kα is 35.3 cm^{-1}, and an 8 × 8 × 10 summation was employed. The range of transmission coefficients (for I) was 0.591–0.639. No correction was made for extinction.

For intensity data collection a θ–2θ scan of 1.5° 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 $0° < 2\theta < 41°$ were examined (1021). Of these, 434 reflections had $I \geq 2\sigma(I)$; these were used for the refinement of the structure. Six reflections were omitted because of obvious setting or reading errors in the manual data collection. Two reflections (012 and 11$-$2) were removed from the data set because their high intensity saturated the counter. Four reflections, measured periodically during the 6-day data collection, indicated there was reasonable crystal and electronic stability while the data were collected ($\Delta I < 2\sigma$).

The standard deviations for I were calculated by $\sigma(I) = (S + BT^2 + 0.0016I^2)^{1/2}$ (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

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[1] D. W. J. Cruickshank, *Acta Crystallogr.*, **9**, 915 (1956).

[2] D. C. Phillips *ibid.*, **9**, 237 (1956).

[3] F. H. Herbstein and G. M. J. Schmidt, *ibid.*, **8**, 399 (1955).

[4] S. N. Sen, *Indian J. Phys.*, **22**, 347 (1948).

[5] P. Marsaw, *Acta Crystallogr., Sect. B*, **27**, 42 (1971); J. J. H. McDowell, *ibid.*, **25**, 2195 (1969).

[6] I. Rowe and B. Post, *Acta Crystallogr.*, **11**, 372 (1958).

[7] S. Hosoya, *ibid.*, **21**, 21 (1966).

[8] S. Hosoya, *ibid.*, **20**, 429 (1966).

[9] See F. G. Mann, "The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony, and Bismuth," 2nd ed, Wiley, 1970, and references therein.

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

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

[12] A. Foust, Program ANGSET, University of Wisconsin, 1969.

[13] A general absorption program written at the University of Wisconsin, which utilizes the method of W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957).

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,[14] and real and imaginary anomalous dispersion corrections were made for As and Cl using the values given by Cromer.[15] All calculations were done with the IBM 360/50 computer at the University of Arkansas Computer Center.[16]

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 two 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 rigid groups using the film data. When the rigid group constraints were removed and all nonhydrogen atoms were refined with isotropic thermal motion, R_1 $(=\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ was 0.08.

In the least-squares refinement using the diffractometer data, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where w is $1/\sigma(F)$ 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 and the arsenic and chlorine atoms were refined with anistropic thermal parameters, R_1 and R_2 became 0.047 and 0.046, respectively. This final refinement consisted of 71 parameters and 434 reflections. In the final cycle of refinement no parameter shifted by more than 0.17σ. The standard deviation of an observation of unit weight is 1.06, and no $\Delta F/\sigma$ values were greater than 3.4.[17] A final difference map did not have any peaks which were interpretable chemically. The largest negative value was -0.34 e/Å^3, and the highest electron density (near the center of the hetero ring) was 0.44 e/Å^3, which is equal to 8% 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.

TABLE I[a]

FINAL ATOMIC POSITIONAL AND ISOTROPIC THERMAL PARAMETERS FOR $C_{12}H_8OAsCl$

Atom	X	Y	Z	B, Å^2
As	0.0879 (3)	0.2704 (1)	0.3673 (1)	
Cl	−0.1231 (9)	0.1451 (3)	0.3838 (4)	
O	−0.3624 (18)	0.3883 (7)	0.3962 (9)	4.6 (3)
C(1)	0.058 (3)	0.335 (1)	0.483 (1)	2.4 (4)
C(2)	0.256 (3)	0.332 (1)	0.578 (1)	3.8 (4)
C(3)	0.244 (3)	0.375 (1)	0.664 (1)	4.0 (4)
C(4)	0.025 (3)	0.421 (1)	0.660 (1)	4.0 (4)
C(5)	−0.170 (3)	0.425 (1)	0.569 (1)	3.0 (4)
C(6)	−0.149 (3)	0.380 (1)	0.485 (1)	3.0 (4)
C(7)	−0.181 (3)	0.335 (1)	0.266 (1)	3.0 (4)
C(8)	−0.362 (3)	0.379 (1)	0.296 (1)	3.0 (4)
C(9)	−0.558 (3)	0.421 (1)	0.222 (1)	3.3 (4)
C(10)	−0.568 (3)	0.421 (1)	0.121 (1)	4.5 (4)
C(11)	−0.387 (3)	0.380 (1)	0.093 (1)	4.5 (4)
C(12)	−0.194 (3)	0.333 (1)	0.165 (1)	4.0 (4)
H(1)[b]	0.405	0.300	0.581	5.0
H(2)	0.380	0.373	0.726	5.0
H(3)	0.018	0.450	0.722	5.0
H(4)	−0.315	0.456	0.565	5.0
H(5)	−0.353	0.379	0.368	5.0
H(6)	−0.398	0.381	0.021	5.0
H(7)	−0.702	0.451	0.072	5.0
H(8)	−0.680	0.451	0.243	5.0

[a] In all of the tables the numbers in parentheses are estimated standard deviations in the least significant digit(s) of the preceding parameter. [b] The H atom positions were calculated from the C positions, and the isotropic temperature factors were assigned values of 5.0. None of these H atom parameters was included in the least-squares refinement.

TABLE II

ANISOTROPIC THERMAL PARAMETERS FOR As AND Cl IN $C_{12}H_8OAsCl$[a]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
As	345 (8)	48 (1)	106 (2)	−2 (4)	70 (3)	3 (1)
Cl	580 (23)	47 (3)	100 (5)	−35 (7)	65 (8)	0 (3)

Root-Mean-Square Vibration Amplitudes (Å)

Atom	Maximum	Intermediate	Minimum
As	0.30	0.23	0.22
Cl	0.32	0.29	0.21

[a] The anisotropic thermal parameter used was $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

TABLE III

SELECTED INTRAMOLECULAR DISTANCES AND ANGLES IN $C_{12}H_8OAsCl$

Atom	Dist, Å	Atom	Angle, deg
As–Cl	2.255 (5)	Cl–As–C(1)	96.7 (5)
As–C(1)	1.92 (2)	Cl–As–C(7)	98.2 (5)
As–C(7)	1.95 (2)	C(1)–As–C(7)	94.6 (7)
O–C(6)	1.42 (2)	As–C(1)–C(6)	125.3 (7)
O–C(8)	1.39 (2)	As–C(7)–C(8)	120.3 (9)
C(1)–C(2)	1.42 (2)	O–C(6)–C(1)	122 (2)
C(2)–C(3)	1.37 (2)	O–C(8)–C(7)	126.2 (9)
C(3)–C(4)	1.41 (2)	C(6)–O–C(8)	124 (1)
C(4)–C(5)	1.38 (3)	C(1)–C(2)–C(3)	122 (2)
C(5)–C(6)	1.36 (2)	C(2)–C(3)–C(4)	119 (1)
C(6)–C(1)	1.37 (2)	C(3)–C(4)–C(5)	120 (1)
C(7)–C(8)	1.39 (2)	C(4)–C(5)–C(6)	118 (1)
C(8)–C(9)	1.38 (2)	C(5)–C(6)–C(1)	125 (1)
C(9)–C(10)	1.38 (3)	C(6)–C(1)–C(2)	116 (2)
C(10)–C(11)	1.37 (3)	C(7)–C(8)–C(9)	120 (1)
C(11)–C(12)	1.40 (2)	C(8)–C(9)–C(10)	119 (1)
C(12)–C(7)	1.37 (3)	C(9)–C(10)–C(11)	121 (1)
C–H (assigned)	0.95	C(10)–C(11)–C(12)	121 (1)
		C(11)–C(12)–C(7)	118 (2)
		C(12)–C(7)–C(8)	120 (1)
		Cl–As···O	86.6 (2)
		C–C–H (assigned)	120.0

TABLE IV

ATOMIC DISPLACEMENTS FROM PLANAR ARRANGEMENTS IN $C_{12}H_8OAsCl$[a]

Distance (Å) from Least-Squares Plane A

As	−0.02	C(2)	0.00	C(5)	0.00
O	0.00	C(3)	0.00	C(6)	−0.01
C(1)	0.03	C(4)	−0.02		

Distance (Å) from Least-Squares Plane B

As	0.03	C(8)	0.01	C(11)	−0.04
O	−0.04	C(9)	0.04	C(12)	0.00
C(7)	−0.01	C(10)	0.01		

[a] Each atom whose distance to a plane is listed was used with unit weight in the calculation of that plane.

The final positional and isotropic thermal parameters are given in Table I, and Table II gives the final anisotropic thermal parameters. Table III lists the intramolecular distances and angles, and Table IV gives atom displacements from the two most prominent molecular planes.

Discussion

The 10-chlorophenoxarsine molecule is folded 156.3° on the As···O axis, as shown in Figure 1. The OAsCl plane makes a 79.6° angle with the OAs(C_1–C_6) side of the molecule and a 76.6° angle with the OAs(C_7–C_{12})

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[14] D. T. Cromer and J. T. Waber, Los Alamos Scientific Laboratory, private communication.

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

[16] In addition to local systems programs modifications of the following programs were used: Johnson's ORTEP thermal ellipsoid plot program, Zalkin's FORDAP Fourier program, and the Busing–Levy ORFLS least-squares program. σ's for bond distances and angles were calculated using the diagonal elements of the error matrix.

[17] 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-72-1846. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

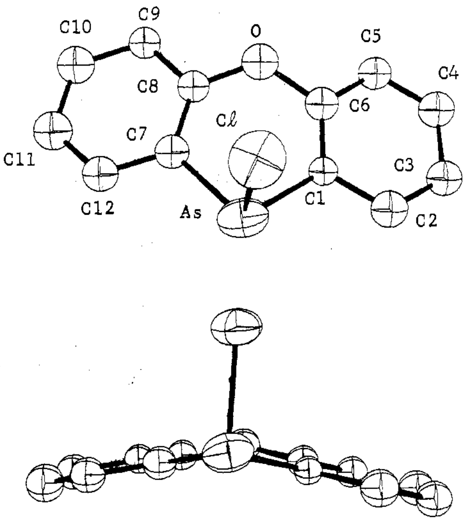

Figure 1.—ORTEP drawings of 10-phenoxarsine chloride, showing anisotropic thermal ellipsoids.

side of the molecule (although the As and O atoms are displaced as much as 10σ and 4σ from the *o*-phenylene planes, the small distances involved (0.02–0.04 Å) lead us to consider these units planar). The chlorine atom is on the outside of the folded unit, with an O···As–Cl angle of 86.6 (2)°. The As–C distances of 1.92 (2) and 1.95 (2) Å and the As–Cl distance of 2.255 (5) Å compare closely with the corresponding distances of 1.908 (9), 1.93 (1), and 2.301 (4) Å found by Trotter[10] for phenarsazine chloride (NH in place of O). Both As–Cl distances (in phenoxarsine and phenarsazine) are longer than that found in arsenic trichloride[18] (2.161 (4) Å) but are comparable to the value found for chlorodiphenylarsine[19] (2.26 (2) Å). The As–C bonds are slightly shorter than the 1.99 (2) Å value found for $(CH_3)_2As(S)SAs(CH_3)_2$,[20] for example. The average value for the two C–O distances found for 10-chlorophenoxarsine is comparable with the 1.36 (1) Å distance considered normal for an aromatic-C to O bond.[21]

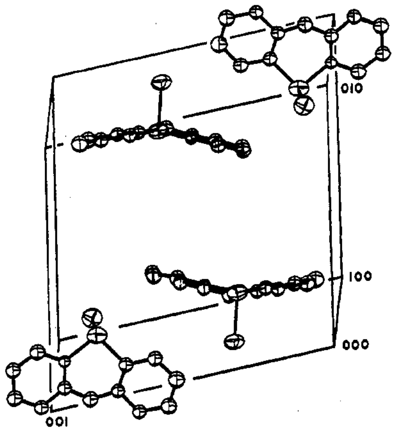

Figure 2.—The unit cell of 10-phenoxarsine chloride.

The differences between the phenarsazine molecule and the phenoxarsine molecule are not large, but they all appear to be consistent with the concept that the phenoxarsine moiety has less aromatic character, perhaps as a result of a slightly smaller amount of ionic character, *i.e.*, less contribution from ($C_{12}H_8OAs^+Cl^-$). This rationale is consistent with the less planar structure, the slightly longer As–C and X–C bonds, and the slightly shorter As–Cl bond of 10-phenoxarsine chloride. These would be the expected results obtained by considering either the higher electronegativity of O compared with that of NH (inductive effects) or the poorer ability of the O atom to support the accommodation of the positive charge in the heterocycle (resonance effects).

The crystal packing of 10-phenoxarsine chloride is shown in Figure 2. None of the nonhydrogen contacts is shorter than the corresponding van der Waals distances, and there appears to be no unique feature of the molecular packing.

Acknowledgments.—The authors wish to acknowledge the support of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation's Program of College Teachers Research Participation. We are also grateful to the University of Arkansas for providing computer facilities for this work.

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(18) P. Kisluik and C. H. Townes, *J. Chem. Phys.*, **18**, 1109 (1950).

(19) J. Trotter, *Can. J. Chem.*, **40**, 1590 (1962).

(20) A. Camerman and J. Trotter, *J. Chem. Soc.*, 219 (1963).

(21) L. E. Sutton, *et al.*, "Configuration in Molecules and Ions," *Chem. Soc., Spec. Publ.*, **No. 11** (1958).