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# 10-Chlorophenothiarsenin, $C_{12}H_8AsClS$

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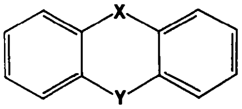
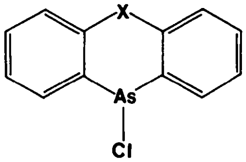
**Abstract.** $M_r = 294{\cdot}63$, monoclinic, $P2_1/n$, $a = 8{\cdot}025\,(2)$, $b = 12{\cdot}113\,(3)$, $c = 11{\cdot}742\,(1)$ Å, $\beta = 92{\cdot}52\,(1)°$, $V = 1140{\cdot}3\,(6)$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}72$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71073 Å, $\mu = 33{\cdot}5$ cm$^{-1}$, $F(000) = 584$, $T = 294$ K. Final $R = 0{\cdot}026$ for 1439 observed reflections. The two nearly planar $C_6H_4AsS$ 'halves' of the heterocycle form a dihedral angle of 152·68 (5)°, and the exocyclic Cl atom is in a quasi-axial position. The As—Cl distance is 2·241 (1) Å and the Cl—As—C, C—As—C and C—S—C angles are 97·1 (1), 99·8 (1) and 107·2 (1)°, respectively.

**Introduction.** One structural feature of interest in heterocyclic molecules of template (1) is the dihedral angle (the 'butterfly angle') between the two $C_6XY$ planes, which intersect at the $X\cdots Y$ line. Fold angles which have been reported cover a wide range: for example, the dihedral angle is 128·1° for $X = Y = \mathrm{S}$ (Rowe & Post, 1958), 138·4° for $X = \mathrm{O}$ and $Y = \mathrm{S}$ (Hosoya, 1966), 158·5° for $X = \mathrm{NH}$ and $Y = \mathrm{S}$ (McDowell, 1976), and 180° for planar aromatic molecules such as anthracene ($X = Y = \mathrm{CH}$) (Cruickshank, 1956), acridine ($X = \mathrm{N}$, $Y = \mathrm{CH}$) (Phillips, 1956), and anthraquinone ($X = Y = \mathrm{CO}$) (Sen, 1948). Several arsenic-containing structures have been reported and they also have shown a variety of dihedral angles, from 117° found in $(C_6H_4)_2As_2Me_2$ (Kennard, Mann, Watson, Fawcett & Kerr, 1968) to the 178·5° value found for the $(C_6H_4)_2OAs$ units in the 'butterfly dimer' $O(C_6H_4)_2As\text{-}S\text{-}As(C_6H_4)_2O$ (Grindstaff, Cordes, Fair, Perry & Handy, 1972). Structures of two molecules of type (2) have been reported: a dihedral angle of 169·3° was found by Camerman & Trotter (1965) for (2) with $X = \mathrm{NH}$, and an angle of 156·3° was found for $X = \mathrm{O}$ (Stuckey, Cordes, Handy, Perry & Fair, 1972). The present report on the molecule of template (2) with $X = \mathrm{S}$ provides an opportunity to extend this series and determine the structural effect of a third period, *d*-orbital element in the $X$ position.



(1)



(2)

**Experimental.** Title crystal prepared by a modification which used thiophenol in place of phenol in the phenoxarsine preparation of Roberts & Turner (1925); suitable crystals obtained by slow cooling of a petroleum ether solution. Yellow parallelepiped crystal, 0·32 × 0·32 × 0·50 mm, mounted with epoxy glue on a glass fiber. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation. 25 reflections with $2\theta$ between 21 and 27° used for least-squares determination of cell constants. Total of 2276 reflections measured using $\theta$–$2\theta$ scans for $2\theta$ from 4 to 50° ($h = 0$ to 6, $k = 0$ to 14, $l = -13$ to 14). $R_{\mathrm{int}} = 0{\cdot}02$. Scan range $(0{\cdot}9 + 0{\cdot}35\tan\theta)°$, scan speeds 2–20° min$^{-1}$. Intensities of four reflections ($0\bar{2}\bar{7}$, $20\bar{6}$, $1\bar{5}\bar{4}$, and $2\bar{6}0$) measured periodically during data collection varied less than 4·2% and thus indicated crystal and electronic stability. 714 reflections with $I < 3\sigma(I)$ considered unobserved. Systematic absences of $h0l$ for $(h+l)$ odd and $0k0$ for $k$ odd uniquely indicate space group $P2_1/n$. Structure solved by analysis of the Patterson map which gave positions of As, S and Cl atoms. All H atoms located on difference maps. Final full-matrix least-squares refinement based on $(|F_o| - |F_c|)^2$ included 168 parameters (positional and anisotropic thermal parameters for all non-H atoms and positional and isotropic thermal parameters for H atoms) for a parameter/reflection ratio of 1:8·6. No absorption or secondary-extinction corrections made. Final $R = 0{\cdot}026$, $R_w = 0{\cdot}030$, $S = 1{\cdot}18$; weighting scheme based on counting statistics ($p = 0{\cdot}03$) gave no systematic variation of $\Delta F/\sigma$ as a function of either $F$ or $\sin\theta$. In final cycle of refinement maximum shift/error 0·01. Final difference map had maximum value 0·4 e Å$^{-3}$. Atomic scattering factors for neutral atoms

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and real and imaginary anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Computer programs used: those of Enraf–Nonius (1979) *SDP* program package.

**Discussion.** Table 1 gives atom coordinates and Table 2 derived distances and angles. Fig. 1 gives two views of the molecule and shows the atom-numbering scheme used; Fig. 2 is a stereoview showing the crystal packing.*

Table 1. *Final fractional coordinates and isotropic thermal parameters with e.s.d.'s in parentheses*

| | $x$ | $y$ | $z$ | $B_{eq}$*/$B_{iso}$ (Å$^2$) |
|---|---|---|---|---|
| As | 0·24378 (4) | 0·08179 (3) | 0·17295 (3) | 3·846 (7) |
| Cl | 0·0621 (1) | −0·00856 (8) | 0·27857 (8) | 5·27 (2) |
| S | 0·5130 (1) | −0·13408 (8) | 0·26415 (8) | 5·16 (2) |
| C(1) | 0·4239 (4) | 0·0881 (3) | 0·2863 (3) | 3·46 (6) |
| C(2) | 0·4490 (4) | 0·1901 (3) | 0·3394 (3) | 4·63 (8) |
| C(3) | 0·5703 (5) | 0·2033 (3) | 0·4252 (3) | 5·72 (9) |
| C(4) | 0·6682 (4) | 0·1158 (4) | 0·4577 (3) | 5·38 (9) |
| C(5) | 0·6497 (4) | 0·0161 (3) | 0·4053 (3) | 4·57 (8) |
| C(6) | 0·5264 (4) | 0·0004 (3) | 0·3182 (3) | 3·57 (7) |
| C(7) | 0·3136 (4) | −0·0433 (3) | 0·0862 (3) | 3·52 (7) |
| C(8) | 0·4224 (4) | −0·1253 (3) | 0·1261 (3) | 3·68 (7) |
| C(9) | 0·4557 (4) | −0·2142 (3) | 0·0559 (3) | 4·58 (8) |
| C(10) | 0·3839 (4) | −0·2193 (3) | −0·0528 (3) | 5·35 (9) |
| C(11) | 0·2816 (5) | −0·1382 (3) | −0·0938 (3) | 5·05 (9) |
| C(12) | 0·2477 (4) | −0·0503 (3) | −0·0258 (3) | 4·19 (8) |
| H(3) | 0·378 (3) | 0·249 (2) | 0·320 (2) | 3·9 (6) |
| H(4) | 0·588 (4) | 0·263 (3) | 0·446 (2) | 6·3 (9) |
| H(5) | 0·756 (4) | 0·126 (3) | 0·517 (3) | 6·0 (8) |
| H(6) | 0·716 (4) | −0·047 (2) | 0·426 (2) | 4·9 (8) |
| H(9) | 0·523 (3) | −0·269 (2) | 0·080 (2) | 4·0 (7) |
| H(10) | 0·407 (3) | −0·270 (2) | −0·089 (2) | 3·7 (6) |
| H(11) | 0·234 (4) | −0·146 (3) | −0·163 (2) | 5·6 (8) |
| H(12) | 0·181 (3) | 0·007 (2) | −0·054 (2) | 3·8 (7) |

* $B_{eq}$= isotropic $B$ values equivalent to the anisotropic ellipsoids $= \frac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{13}ac\cos\beta)$.

Table 2. *Bond distances* (Å) *and angles* (°) *in* $C_{12}H_8SAsCl$

| | | | |
|---|---|---|---|
| As–C(1) | 1·923 (3) | As–C(7) | 1·923 (3) |
| S–C(6) | 1·749 (3) | S–C(8) | 1·750 (3) |
| C(1)–C(6) | 1·386 (4) | C(7)–C(8) | 1·390 (4) |
| C(1)–C(2) | 1·395 (4) | C(8)–C(9) | 1·389 (4) |
| C(2)–C(3) | 1·379 (5) | C(9)–C(10) | 1·379 (5) |
| C(3)–C(4) | 1·364 (6) | C(10)–C(11) | 1·354 (6) |
| C(4)–C(5) | 1·360 (6) | C(7)–C(12) | 1·398 (4) |
| C(5)–C(6) | 1·405 (4) | C(11)–C(12) | 1·366 (5) |
| As–Cl | 2·241 (1) | C–H (range) | 0·77–0·98 |
| As···S | 3·528 (1) | | |
| | | | |
| Cl–As–C(1) | 97·10 (9) | Cl–As–C(7) | 96·90 (9) |
| C(1)–As–C(7) | 99·8 (1) | C(6)–S–C(8) | 107·2 (1) |
| As–C(1)–C(6) | 125·1 (2) | As–C(7)–C(8) | 125·3 (2) |
| As–C(1)–C(2) | 115·7 (2) | As–C(7)–C(12) | 116·0 (2) |
| C(1)–C(2)–C(3) | 120·9 (4) | C(8)–C(7)–C(12) | 118·7 (3) |
| C(2)–C(1)–C(6) | 119·1 (3) | S–C(8)–C(7) | 125·8 (2) |
| C(2)–C(3)–C(4) | 119·6 (4) | S–C(8)–C(9) | 114·8 (3) |
| C(3)–C(4)–C(5) | 120·9 (4) | C(7)–C(8)–C(9) | 119·2 (3) |
| C(4)–C(5)–C(6) | 120·6 (4) | C(8)–C(9)–C(10) | 120·1 (4) |
| C(1)–C(6)–C(5) | 118·9 (3) | C(9)–C(10)–C(11) | 121·2 (4) |
| S–C(6)–C(1) | 126·2 (2) | C(10)–C(11)–C(12) | 119·4 (4) |
| S–C(6)–C(5) | 114·9 (3) | C(7)–C(12)–C(11) | 121·3 (4) |
| C–C–H (range) | 116–123 | S···As–Cl | 82·80 (3) |

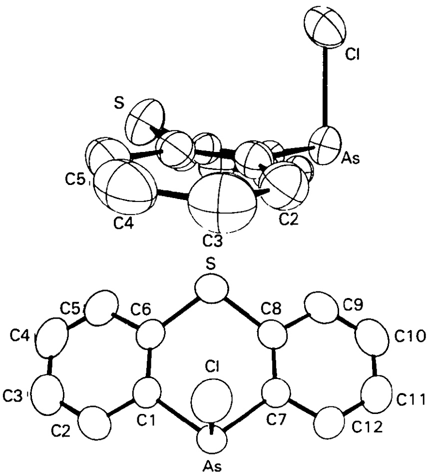

Fig. 1. Two views and the atom-numbering scheme for $C_{12}H_8SAsCl$.

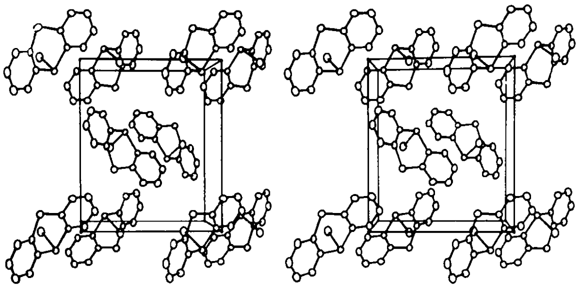

Fig. 2. Crystal packing for $C_{12}H_8SAsCl$. The $z$ axis is horizontal, the $y$ axis vertical, and the origin is in the lower, left, front corner.

The exocyclic Cl atom in $C_{12}H_8SAsCl$ is in the 'axial' position, as was found for $C_{12}H_8OAsCl$ (Stuckey *et al.*, 1972) and $C_{12}H_8(NH)AsCl$ (Camerman & Trotter, 1965). Although the dihedral angle of 152·68 (5)° in the title compound is the smallest reported for this series of axial heterocycles, it is only slightly smaller than the 156·3° value of the corresponding oxygen compound and thus indicates there are no wholesale changes in structure associated with the inclusion of a third period (*d*-orbital) element in the heteroatom position opposite arsenic. The As and S atoms are displaced 0·05 to 0·10 Å out of the phenylene planes [planar to within 0·018 (3) Å] to the chlorine side of the planes; similar displacements have been found for the heavy atoms in most of the molecules of template (2).

The C–As–C angle of 99·8 (1)° is larger than both the 94·6 (7)° value in $(C_6H_4)_2OAsCl$ and the 97·0 (4)° value in $(C_6H_4)_2(NH)AsCl$. Likewise, the C–S–C angle of 107·2 (1)° is larger than the 100·3 (5)° value found for thianthrene [structure (1), $X = Y =$ S] (Rowe & Post, 1958) and is 10° larger than that for phenoxathiin [structure (1), $X =$ O, $Y =$ S] (Hosoya, 1966). To make the molecule completely planar by changing only the angles at the heteroatoms, however,

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* Lists of anisotropic thermal parameters, distances and angles involving H atoms, and $F_o$ *vs* $F_c$ have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38510 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the C—As—C bond angle would have to be increased to 104° and the C—S—C angle would have to be increased to 114°. This additional distortion apparently requires more energy than would be gained by a planar-bonding scheme.

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# Carbonato[tris(2-aminoethyl)amine]cobalt(III) Chloride Trihydrate, $[Co(C_6H_{18}N_4)(CO_3)]Cl.3H_2O$

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**Abstract.** $M_r = 354\cdot7$, monoclinic, $P2_1/c$, $a = 7\cdot177\,(1)$, $b = 19\cdot286\,(2)$, $c = 10\cdot743\,(3)$ Å, $\beta = 93\cdot86\,(4)°$, $V = 1483\cdot6\,(8)$ Å$^3$, $D_m = 1\cdot58\,(1)$, $D_x = 1\cdot588\,(1)$ g cm$^{-3}$, $Z = 4$, $\lambda$(Mo $K\alpha$) = 0·7107 Å, $\mu = 13\cdot6$ cm$^{-1}$, $T = 295\,(1)$ K, $F(000) = 744$. The final discrepancy factors were $R_F = 2\cdot0\%$ and $wR_F = 2\cdot7\%$ for those 1985 reflections $[F_o > 2\sigma(F_o)]$ in the range $3\cdot5° < 2\theta < 47°$. The Co$^{III}$ ion is surrounded by four N atoms from the tetradentate amine ligand and by two O atoms from the chelated carbonate ligand in a somewhat distorted octahedron, *e.g.* the angle O—Co—O = 68·46 (5)°. One of the Co—O bonds is longer than the other, 1·931 (1) and 1·910 (1) Å, which suggests that the bond breaking during decarboxylation preferentially takes place at the site of the longer bond.

**Introduction.** In recent years, many interesting studies on cobalt(III) and chromium(III) complexes containing tris(2-aminoethyl)amine ($\beta,\beta',\beta''$-triaminotriethylamine, tren) as a tetradentate ligand have been undertaken (*e.g.* Dasgupta & Harris, 1971, 1978; Madan, Reiff & Bailar, 1965; Zipp & Madan, 1976) since the tripodal nature of the ligand offers a stereochemically rigid system. It was observed that the acid-catalyzed Co—O bond breaking rate in $[Co(tren)CO_3]^+$ is larger than that for the corresponding ethylenediamine and tetraammine analogues (Dasgupta & Harris, 1971). It was also observed that *cis*-$[Co(tren)Cl_2]^+$ aquates much more rapidly than other dichlorocobalt(III) complexes containing organic amines. The enhancement of rate has been attributed to steric strains produced by the peculiar geometry of the complex (Madan, Reiff & Bailar, 1965). X-ray diffraction study of the complex $[Ni(tren)(NCS)_2]$ has shown that the bonds between the metal and the primary amine nitrogens are drawn back towards the tertiary N atom (Rasmussen, 1959). Hence we were interested in finding the crystal structure of $[Co(tren)CO_3]^+$ which might give us some clue about the reactivity of this complex.

**Experimental.** $[Co(tren)CO_3]ClO_4$ was prepared following the published procedure (Dasgupta & Harris, 1978). A saturated solution of sodium chloride was added to a solution of $[Co(tren)CO_3]ClO_4$ with stirring. The resultant solution was left at 293 K for several hours, after which bright-red crystals appeared which

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