

5,10-Dihydro-5,10-dimethyloctafluoroarsanthrene

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Abstract. $C_{14}H_6F_8As_2$, $M_r = 476.02$, triclinic, space group $P\bar{1}$, $a = 8.121(5)$, $b = 8.178(5)$, $c = 6.909(4)$ Å, $\alpha = 97.23(4)^\circ$, $\beta = 118.16(4)^\circ$, $\gamma = 107.48(4)^\circ$, $V = 365.8$ Å³, $Z = 1$, $D_c = 2.161$, $D_o = 2.14$ g cm⁻³, $\mu(Mo K\alpha) = 49.1$ cm⁻¹. A molecule with a crystallographic centre of symmetry gave a final R of 0.073 for 835 counter reflexions. The molecule is planar except for the methyl groups, which are *trans*; this is in contrast to the non-fluorinated analogue [Kennard, Mann, Watson, Fawcett & Kerr, *Chem. Commun.* (1968), pp. 269–271] which has a ‘butterfly’ conformation with the methyl groups *cis*.

Introduction. Recrystallization from hexane gave colourless plates (Cullen & Wu, 1976). Photographs (Cu $K\alpha$ radiation) showed the crystals to be triclinic. A crystal (0.08 × 0.15 × 0.30 mm) was used to measure the cell dimensions and intensities on a Picker FACS-I four-circle diffractometer. The unit-cell dimensions were determined by least-squares refinement of setting angles of nine reflexions with $2\theta > 25^\circ$. Intensities were collected with Nb-filtered Mo $K\alpha$ radiation ($\lambda K\alpha_1 = 0.70926$ Å) and a scintillation counter with pulse-height discrimination. A θ – 2θ scan was used with a scan base-width of 1.5° (increased for dispersion) and scan speed of 2° min⁻¹. Background measurements of 20 s were taken at each of the scan limits. The intensities of 967 unique reflexions with $2\theta < 45^\circ$ were measured of which 835 were regarded as observed [$I > 2.3\sigma(I)$ where $\sigma(I)$ is the standard deviation derived from counting statistics]. Corrections were applied for Lorentz–polarization effects but not for absorption.

Intensity statistics indicated a centric distribution and the space group was assumed to be $P\bar{1}$. An ordered structure with one molecule in the unit cell requires the molecule to have $\bar{1}$ symmetry. A Patterson function gave the position of the As atom; the C and F atoms were located from a difference synthesis. Least-squares refinement with isotropic temperature parameters reduced $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ to 0.106. Refinement with anisotropic temperature parameters reduced R to 0.085 and a difference synthesis indicated the positions of the H atoms. Inclusion of the H atoms gave a final R of 0.073 after refinement of the non-hydrogen parameters.

The weighting scheme was $w = 1/\sigma(F)^2$ where $\sigma(F)$ is the standard deviation in F . Scattering factors were taken from Cromer & Waber (1965) except for H for which the values from Stewart, Davidson & Simpson (1965) were used. The programs have been described by Einstein & Jones (1972).

Final atomic parameters are shown in Table 1.† Bond distances and angles are listed in Table 2 with those for 5,10-dihydro-5,10-dimethylarsanthrene. A perspective view of the molecule and atom labelling are shown in Fig. 1.

Discussion. Apart from the methyl groups the atoms of the molecule are approximately coplanar; deviations from the least-squares plane through one of the benzene rings are listed in Table 3. This is in contrast to 5,10-dihydro-5,10-dimethylarsanthrene (Kennard *et al.*, 1968), in which the molecule has *mm* symmetry and is folded about the As–As axis giving a ‘butterfly’ conformation with the methyl groups *cis*. The angle be-

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32682 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Final atomic parameters

Atomic fractional coordinates and their estimated standard deviations (in parentheses) are multiplied by 10⁴ for the As atom and by 10³ for the remaining atoms.

	<i>x</i>	<i>y</i>	<i>z</i>
As	119 (2)	2302 (2)	–528 (3)
F(1)	254 (1)	302 (1)	–256 (2)
F(2)	418 (1)	116 (1)	–400 (2)
F(3)	374 (1)	–215 (1)	–358 (2)
F(4)	173 (2)	–359 (1)	–165 (2)
C(1)	229 (2)	135 (2)	–229 (2)
C(2)	315 (2)	43 (2)	–304 (2)
C(3)	292 (2)	–125 (2)	–285 (2)
C(4)	191 (2)	–190 (2)	–185 (2)
C(5)	106 (2)	–99 (2)	–102 (2)
C(6)	130 (2)	72 (2)	–127 (2)
C(7)	259 (3)	398 (2)	220 (3)
H(1)	353	463	188
H(2)	250	490	300
H(3)	322	342	318

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tween the two benzene ring planes is 117° . Only the *cis* isomer was reported for the dimethyl derivative but for the di-*p*-tolyl derivative and for the related 5,10-diethyl-5,10-dihydrophosphanthrene both *cis* and *trans* isomers were reported. For 5,10-dihydro-5,10-dimethyloctafluoroarsanthrene only one isomer is present (Cullen & Wu, 1976).

The planar configuration for 5,10-dihydro-5,10-dimethyloctafluoroarsanthrene would appear to result from steric interference between F atoms at the 1, 4, 6,

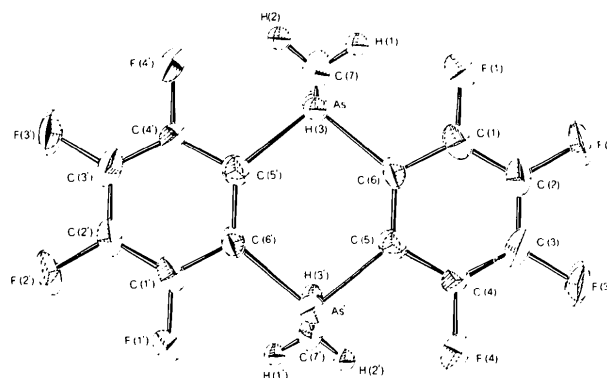


Fig. 1. Perspective view of 5,10-dihydro-5,10-dimethyloctafluoroarsanthrene drawn by ORTEP (Johnson, 1965). The thermal ellipsoids are shown with 50% probability.

Table 2. Bond distances (Å) and angles ($^\circ$) and their standard deviations for (i) 5,10-dihydro-5,10-dimethyloctafluoroarsanthrene and (ii) 5,10-dihydro-5,10-dimethylarsanthrene

Bond distances	(i)	(ii)
As—C(7)	1.89 (2)	1.953 (6)
As—C(5')	1.96 (1)	1.953 (3)
As—C(6)	1.97 (1)	1.953 (3)
C(1)—C(6)	1.34 (2)	1.393 (4)
C(1)—C(2)	1.38 (2)	1.386 (5)
C(2)—C(3)	1.36 (2)	1.368 (7)
C(3)—C(4)	1.34 (2)	1.386 (5)
C(4)—C(5)	1.39 (2)	1.393 (4)
C(5)—C(6)	1.40 (2)	1.401 (5)
C(1)—F(1)	1.36 (2)	
C(2)—F(2)	1.35 (2)	
C(3)—F(3)	1.33 (2)	
C(4)—F(4)	1.38 (2)	
C(7)—H(1)	0.93	
C(7)—H(2)	0.92	
C(7)—H(3)	0.91	
Bond angles	(i)	(ii)
C(6)—As—C(7)	96.2 (6)	100.2 (2)
C(5')—As—C(7)	96.5 (7)	100.2 (2)
C(5')—As—C(6)	101.2 (5)	95.0 (1)
As—C(6)—C(5)	127 (1)	118.6 (2)
As—C(6)—C(1)	113 (1)	122.0 (2)
C(1)—C(6)—C(5)	119 (1)	119.4 (3)
As'—C(5)—C(6)	131 (1)	118.6 (2)
As'—C(5)—C(4)	113 (1)	122.0 (2)
C(4)—C(5)—C(6)	116 (1)	119.4 (3)
C(3)—C(4)—C(5)	125 (1)	120.3 (3)
C(3)—C(4)—F(4)	117 (1)	
C(5)—C(4)—F(4)	119 (1)	
C(2)—C(3)—C(4)	118 (1)	120.4 (3)
C(2)—C(3)—F(3)	120 (1)	
C(4)—C(3)—F(3)	122 (1)	
C(1)—C(2)—C(3)	119 (1)	120.4 (3)
C(1)—C(2)—F(2)	121 (1)	
C(3)—C(2)—F(2)	120 (1)	
C(2)—C(1)—C(6)	123 (1)	120.3 (3)
C(6)—C(1)—F(1)	120 (1)	
C(2)—C(1)—F(1)	117 (1)	
As—C(7)—H(1)	112	
As—C(7)—H(2)	116	
As—C(7)—H(3)	112	
H(1)—C(7)—H(2)	101	
H(1)—C(7)—H(3)	106	
H(2)—C(7)—H(3)	109	

Table 3. Deviations of atoms (Å) from the least-squares plane through C(1), C(2), C(3), C(4), C(5) and C(6)

The equation of the plane referred to orthogonal axes is $-0.4229x - 0.1382y - 0.8956z - 0.0012 = 0$. The orthogonal system of axes has x along a , y in the ab plane, and z along c^* .

C(1)	0.01	C(1')	-0.02
C(2)	-0.01	C(2')	0.01
C(3)	0.00	C(3')	-0.01
C(4)	0.00	C(4')	-0.01
C(5)	0.00	C(5')	0.00
C(6)	0.00	C(6')	0.00
As	0.14	As'	-0.14
F(1)	0.02	F(1')	-0.02
F(2)	-0.03	F(2')	0.03
F(3)	-0.02	F(3')	0.01
F(4)	0.00	F(4')	0.00
C(7)	-1.68	C(7')	1.68

$$\chi^2 = 1.95.$$

and 9 positions and the methyl groups. Calculations for 5,10-dihydro-5,10-dimethylarsanthrene (Kennard & Motherwell, 1976), generating theoretical F positions (assuming a C—F bond distance of 1.30 Å), indicate contacts of the type $F \cdots C(\text{methyl})$ ca 2.6 Å and $F \cdots H(\text{methyl})$ ca 2.2 Å for a 'butterfly' structure. In the planar structure the corresponding contact distances are $F(1) \cdots C(7) = 3.26$, $F(1) \cdots H(1) = 2.80$, $F(4) \cdots C(7') = 3.25$, and $F(4) \cdots H(1) = 2.88$ Å. There are no particularly short intermolecular contacts.

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***cis*-Tetracarbonyl-1,4-*h*²-1,2-bis(phenylphosphino-1,2-dimethyl)disilanemolybdenum(0)**

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Abstract. $C_{20}H_{24}O_4Si_2P_2Mo$, monoclinic, $C2/c$, $a = 13.375$ (4), $b = 11.101$ (2), $c = 17.250$ (9) Å, $\beta = 92.94$ (2)°, $M_r = 542.5$, $Z = 4$, $D_x = 1.41$ g cm⁻³. The molecule possesses crystallographic C_2 symmetry with octahedral coordination at Mo; the phenyl substituents at the ring P atoms are therefore *trans* to one another. The five-membered chelate ring is non-planar, the Si–Si bond being twisted out of the PMoP' plane by 28.7°. Bond lengths include Mo–P 2.550 (1), P–Si 2.266 (1) and Si–Si 2.378 (1) Å.

Introduction. Cell dimensions were determined by a least-squares fit to settings for 15 reflexions ($\pm hkl$) on a Syntex $P2_1$ four-circle diffractometer (Mo $K\alpha$, $\lambda = 0.71069$ Å). The intensities from a prismatic crystal sealed in a Lindemann-glass capillary were collected on the diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Measurements were carried out in the θ – 2θ mode ($3.0 \leq 2\theta \leq 65.0^\circ$) at scan speeds varying linearly between $2.55^\circ \text{ min}^{-1}$ (150 c.p.s. and below) and $29.3^\circ \text{ min}^{-1}$ (3000 c.p.s. and above). Scan and background times were equal. Three standard reflexions showed no significant variations. Lorentz and polarization but no absorption [$\mu(\text{Mo } K\alpha) = 6.70 \text{ cm}^{-1}$] corrections were applied. 3173 reflexions were retained for use in the structure analysis, after application of the criterion $F \geq 3.0\sigma(F)$ (based on counting statistics).

The structure was solved by Patterson and Fourier methods. Refinement with anisotropic temperature factors for all the non-hydrogen atoms and isotropic temperature factors for the H atoms was by full-matrix least squares, $\Sigma w\Delta^2$ being minimized. The terminal

value of $R_G = [\Sigma w\Delta^2/\Sigma wF_o^2]^{1/2}$ was 0.057, with $R_w = \Sigma w^{1/2}\Delta/\Sigma w^{1/2}F_o = 0.052$ and $R = 0.059$.† The weights were given by $w = k/[\sigma^2(F_o) + gF_o^2]$, where k and g refined to 1.8757 and 0.000524 respectively. In the final cycle the largest observed shift/e.s.d. was 0.002. Complex neutral-atom scattering factors (Cromer & Waber, 1965; Cromer & Liberman, 1970) were employed. Positional parameters and, for H, isotropic thermal parameters are given in Tables 1 and 2. Bond lengths and angles are in Tables 3 and 4.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32683 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Positional parameters* ($\times 10^4$) *for the nonhydrogen atoms*

	x	y	z
Mo	5000	6393 (1)	2500
P	3760 (1)	4761 (1)	2088 (1)
Si	4442 (1)	2905 (1)	1956 (1)
C(1)	5647 (3)	6369 (3)	1458 (2)
O(1)	6014 (2)	6360 (3)	880 (1)
C(2)	5932 (3)	7649 (3)	2913 (2)
O(2)	6445 (3)	8387 (3)	3167 (2)
C(3)	2884 (2)	4944 (3)	1244 (2)
C(4)	3122 (3)	5670 (4)	632 (2)
C(5)	2470 (4)	5778 (5)	9985 (2)
C(6)	1574 (4)	5194 (5)	9954 (3)
C(7)	1322 (4)	4489 (5)	555 (3)
C(8)	1975 (3)	4372 (4)	1210 (3)
C(9)	3483 (5)	1689 (4)	1974 (5)
C(10)	5116 (6)	2916 (6)	1037 (3)

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