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SHORT COMMUNICATION

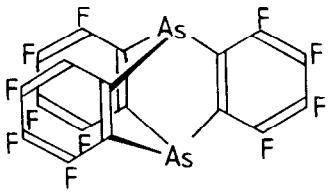
The Crystal and Molecular Structure of Octafluoro-5,10-epoxy-5,10-dihydroarsanthrene, $As_2(C_6F_4)_2O$.

D.S.BROWN, A.G.MASSEY and T.K.MISTRY

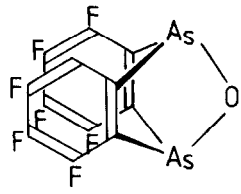
Department of Chemistry, University of Technology, Loughborough, Leics., LE11 3TU;(U.K.)

We have reported [1] the preparation of dodecafluoro-5,10-o-benzeno-arsanthrene (I) and -stibanthrene using the direct method of heating either arsenic or antimony with $1,2\text{-}I_2C_6F_4$. Cullen and Wu made the same compounds via the more conventional, but less convenient, route of treating $AsCl_3$ or $SbCl_3$ with 1,2-dilithiotetrafluorobenzene [2].

When the arsenic used in our direct synthesis contained arsenious oxide a compound having a parent ion at $^m/e = 462$ in its mass spectrum was found to contaminate the dodecafluoro-5,10-o-benzenoarsanthrene; fractional crystallization from 60-80° petroleum ether allowed the isolation of this material. The parent ion in the mass spectrum corresponds to $As_2(C_6F_4)_2O^+$ and other significant ions were identified as $C_{12}F_8^+$, $C_{12}F_6^+$, $AsC_6F_4^+$, AsF_2^+, $C_6F_2^+$ and AsO^+. In the infrared spectrum there were no peaks between 850 and 1000 cm^{-1} suggesting that the two C_6F_4 groups in the molecule are not coupled together, as ortho-linked C_6F_4 groups invariably give a peak of medium intensity at approximately 950 cm^{-1}. The compound was, therefore, tentatively assumed to be octafluoro-5,10-epoxy-5,10-dihydroarsanthrene (II); an X-ray study of single crystals grown from diethyl ether confirmed this deduction.



(I)



(II)

The figure shows the molecular structure and atom numbering for the two crystallographically non-equivalent molecules. There are no significant structure differences between the two molecules, both adopting a 'butterfly' conformation. The average of the eight measured As-C bond lengths is 1.97 ± 0.02 Å and that of the four As-O bonds. 1.81 ± 0.01 Å; As----As intramolecular distances are 2.973(3) and 2.979(3) Å. Bond angles involving As are shown in Table 1, all angles being close to 90°. The bond lengths and angles in the aromatic ring are normal and require no special comment. All these values and the 'butterfly' conformation of the molecule closely resemble those found in the hydrogen analogue [3].

TABLE 1

Bond Angles involving arsenic (standard deviations in brackets)

C(1) -As(1)-O(1)	90.5(11)	C(13)-As(3)-O(2)	88.6(17)
C(6) -As(2)-O(1)	90.1(10)	C(18)-As(4)-O(2)	89.6(8)
C(7) -As(2)-C(6)	92.3(10)	C(19)-As(4)-C(18)	92.8(7)
C(7) -As(2)-O(1)	88.9(10)	C(19)-As(4)-O(2)	89.2(8)
C(12)-As(1)-C(1)	91.4(11)	C(24)-As(3)-C(13)	93.2(18)
C(12)-As(1)-O(1)	89.3(10)	C(24)-As(3)-O(2)	88.8(14)

Partially oxidised arsenic powder was heated at 250°C for 18 h. in a sealed, evacuated tube with an equal weight of 1,2-diiodotetrafluorobenzene. Extraction of the products with 60-80° petroleum ether, followed by fractional crystallization, gave octafluoro-5,10-epoxy-5,10-dihydroarsanthrene, m.pt. 161-162°C. The colourless compound is soluble in all the common organic solvents but is insoluble in water.

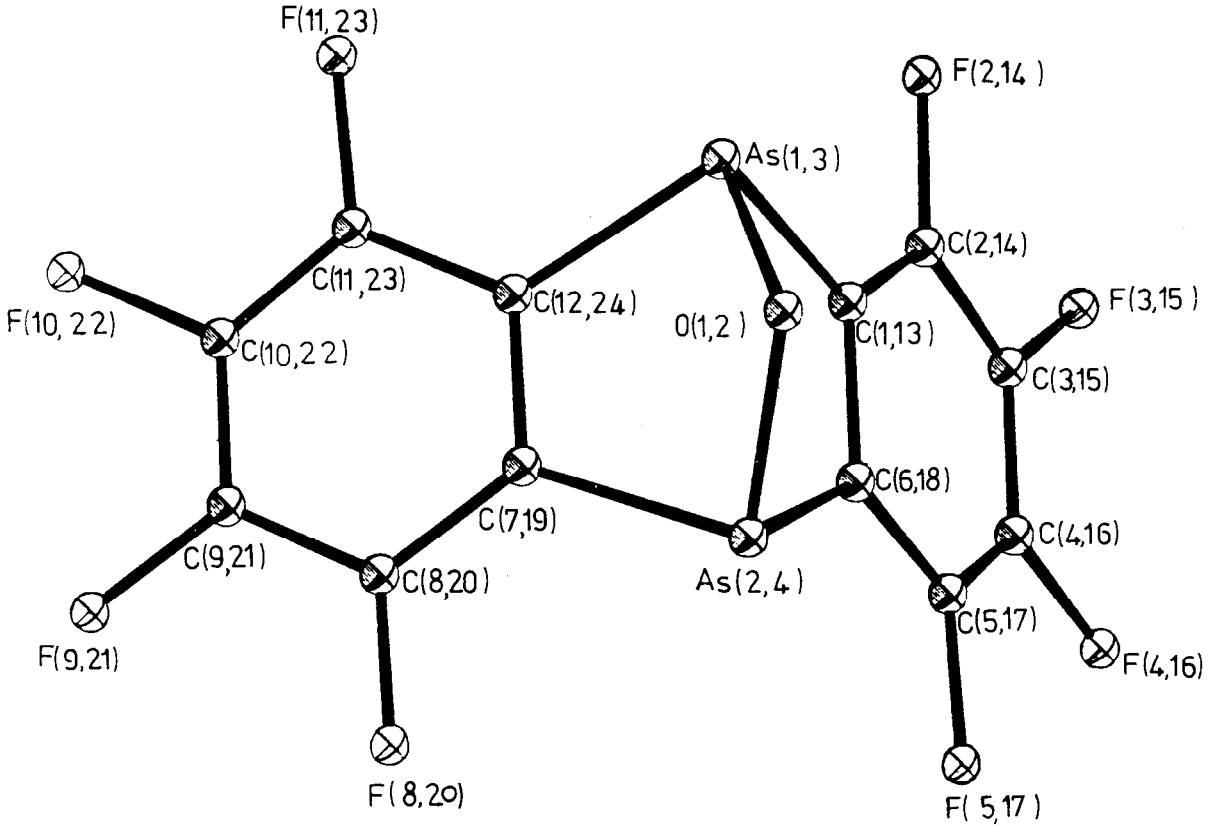


Figure 1. The molecular structure and atom numbering system for the two crystallography non-equivalent but structurally similar molecules.

Attempts to make the antimony analogue by heating dodecafluoro-5,10-o-benzenostibanthrene with water vapour at temperatures upto 300°C in sealed, evacuated tubes failed.

Crystal data $C_{12}As_2F_8O$, M = 461.96; monoclinic, a = 26.660(5), b = 19.220(5) c = 4.990(5) Å, β = 90.3(1)°, U = 2556.90 Å^3, Z = 8, D_c = 2.401 Mg m^{-3}. Space group $P2_1/_n$ with two crystallographically non-equivalent molecules present in the unit cell.

The selected crystal was mounted about the c axis and the intensities of 1563 reflexions, for which $I/\sigma(I)>3$, measured on a Stoë two-circle diffractometer. After corrections for Lorentz and polarisation effects the structure was solved by direct methods and refined by full-matrix least-squares methods to a final conventional R factor of 6.6%. Final positional co-ordinates with their e.s.d.'s are shown in Table 2.

TABLE 2

Positional parameters and their standard deviations (x 10^4)

	x	y	z
As(1)	7178(1)	9612(1)	3168(5)
As(2)	7915(1)	8720(1)	6045(5)
As(3)	1193(1)	2096(1)	8992(5)
As(4)	5310(1)	2262(1)	6668(5)
C(1)	2432(7)	-122(9)	4102(40)
C(2)	2561(8)	4173(11)	1444(46)
C(3)	2144(8)	8906(12)	1661(48)
C(4)	1809(7)	9287(11)	410(44)
C(5)	1763(8)	-7(11)	960(45)
C(6)	2072(7)	291(10)	2764(42)
C(7)	2221(7)	6398(11)	2166(42)
C(8)	2045(8)	6874(11)	4134(48)
C(9)	3451(8)	1915(11)	470(46)
C(10)	1212(9)	6525(12)	3374(48)
C(11)	1373(8)	6055(12)	1467(50)
C(12)	1880(7)	5994(10)	929(42)

(continued on facing page)

TABLE 2 *(cont.)*

C(13)	9464(7)	8277(10)	2249(42)
C(14)	5458(7)	3750(11)	818(44)
C(15)	4974(8)	3970(11)	180(46)
C(16)	4587(8)	3663(11)	1381(44)
C(17)	4657(9)	3174(12)	3272(49)
C(18)	9869(7)	7969(10)	1050(40)
C(19)	9374(7)	6648(10)	1013(40)
C(20)	9516(8)	6002(11)	1847(45)
C(21)	9262(7)	5650(10)	3713(41)
C(22)	3863(8)	9084(11)	-198(46)
C(23)	8699(7)	6563(10)	4143(43)
C(24)	8959(7)	6956(9)	2281(40)
F(2)	2769(4)	8776(6)	4929(25)
F(3)	2170(5)	8217(7)	1090(28)
F(4)	8498(5)	985(7)	1462(29)
F(5)	3592(4)	5367(6)	5336(24)
F(8)	2376(5)	7295(7)	5406(27)
F(9)	8614(5)	2610(8)	3496(30)
F(10)	4286(5)	1584(7)	1106(30)
F(11)	3965(4)	665(6)	4864(25)
F(14)	854(4)	903(6)	4620(25)
F(15)	-88(5)	553(8)	3236(30)
F(16)	888(6)	8880(8)	4290(32)
F(17)	751(5)	7899(7)	566(27)
F(20)	5073(4)	714(7)	4380(26)
F(21)	5584(5)	3(7)	533(28)
F(22)	1404(5)	4424(7)	3272(27)
F(23)	1714(4)	3150(7)	4689(26)
O(1)	7688(5)	8988(7)	2782(27)
O(2)	902(5)	2316(7)	2163(27)

1 C. M. Woodard, G. Hughes and A. G. Massey, J. Organometal. Chem., 112 (1976) 9.

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3 O. Kennard, D. L. Wampler, J. C. Coppola, W. D. S. Motherwell, F. G. Mann, D. G. Watson, C. H. MacGillavry, C. H. Stam and P. Benci, J. Chem. Soc. (C), 1971, 1511.