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Spectral and X-ray studies on 1,6-disubstituted triptycenes

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Mass and NMR spectral data are presented for a number of dodecafluoro-1,6-disubstituted triptycenes. The epoxide $OAs_2(C_6F_4)_2$ can be made by heating together arsenic (As), arsenic(III) oxide (As_2O_3) and 1,2-di-iodotetrafluorobenzene ($1,2\text{-}I_2C_6F_4$) in a sealed tube. The molecular structure of $As_2(C_6F_4)_3$ has been confirmed by X-ray crystallography.

Keywords: Substituted triptycenes, arsenic-triptycenes, antimony-triptycenes, phosphorus-triptycenes, bismuth-triptycenes, mass spectra, NMR

INTRODUCTION

A variety of elements which can achieve pyramidal coordination should be able to act as 'bridgehead' atoms in the 1,6-positions of triptycene but to date only Group IV (carbon, silicon) and Group V (nitrogen, phosphorus, arsenic, antimony, bismuth) derivatives have been isolated.[1] We previously synthesized several dodecafluorotriptycenes having silicon or Group V elements as 1,6-heteroatoms[2,3] and we now describe some of their spectral properties as well as an X-ray structure determination of $As_2(C_6F_4)_3$.

Although their preparation is difficult to accomplish in many cases, once formed the disubstituted fluorotriptycenes are very robust; $Sb_2(C_6F_4)_3$ is unaffected by boiling concentrated hydrochloric acid and suffers only oxidation, not degradation, on dissolution in boiling nitric acid. The corresponding arsenic derivative appears to be insoluble in, and unaffected by, hot nitric acid; neither does it react with refluxing methyl iodide, iodine in boiling carbon tetrachloride (CCl_4) and boiling water–iodine–carbon tetrachloride ($H_2O{-}I_2{-}CCl_4$) mixtures. Furthermore, the crystals of $As_2(C_6F_4)_3$ used in the X-ray studies were grown by sublimation in air at about 100°C over a period of many weeks. As might be expected, the least stable fluorinated triptycene is the bismuth derivative $Bi_2(C_6F_4)_3$. Thus although $Bi_2(C_6F_4)_3$ is unaffected by boiling water, hot concentrated nitric acid causes complete decomposition; chlorine at room temperature cleaves the phenylene groups from bismuth forming bismuth(III) chloride ($BiCl_3$) which was identified as its hydrolysis product, the oxychloride (BiOCl).

When $As_2(C_6F_4)_3$ is made by heating arsenic and $1,2\text{-}I_2C_6F_4$ together in a sealed evacuated tube, tiny amounts of $OAs_2(C_6F_4)_2$ are always present in the product; this epoxide was first identified by its mass spectrum and then the structure confirmed later (Fig. 1) by X-ray crystallography.[4] We have studied this synthesis in more detail to determine if the epoxide arises from arsenic trioxide impurity present in elemental arsenic. Pure As_2O_3 apparently undergoes little or no reaction with $1,2\text{-}I_2C_6F_4$ but when arsenic is added to the mixture both $OAs_2(C_6F_4)_2$ and $As_2(C_6F_4)_3$ are formed in good yield; the two components are readily separable by thin-layer chromatography on alumina using petroleum ether as the solvent.

Mass spectra

The mass spectrum of $OAs_2(C_6F_4)_2$ shows several metastable peaks including those for the transitions $M^+ - AsO$, $As(C_6F_4)_2^+ - As$, $As(C_6F_4)_2^+ - AsF_2$ and $AsC_6F_4{}^+ - C_6F_2$, (M = molecular ion); the base peak in the spectrum is due to the ion $As(C_6F_4)_2^+$.

The mass spectrum of $P_2(C_6F_4)_3$ has a relatively intense doubly-charged parent ion as well as a tiny peak which probably corresponds to the M^{3+} ion; a very strong metastable peak at 389.6 mu is due to the transition $M^+ - 2P$. The doubly-charged parent is also

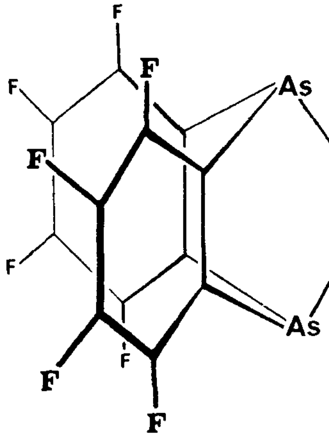


Figure 1 Structure of the epoxide $OAs_2(C_6F_4)_2$.

present in the mass spectrum of $As_2(C_6F_4)_3$ together with metastable peaks for the following transitions:

Parent		Daughter
$As_2(C_6F_4)_3^+$	$\xrightarrow{-2As}$	$C_{18}F_{12}^+$ at 331.9 mu
$As_2(C_6F_4)_3^+$	$\xrightarrow{-As(C_6F_4)_2}$	$AsC_6F_4^+$ at 83.7 mu
$(M\text{-}AsF_2)^+$	$\xrightarrow{-AsF_2}$	$C_{18}F_8^+$ at 281.5 mu
$As(C_6F_4)_2^+$	$\xrightarrow{-As}$	$C_{12}F_8^+$ at 236.2 mu
$As(C_6F_4)_2^+$	$\xrightarrow{-AsF_2}$	$C_{12}F_6^+$ at 179.4 mu
$C_{12}F_6^+$	$\xrightarrow{-F}$	$C_{12}F_5^+$ at 221.4 mu
$C_{12}F_6^+$	$\xrightarrow{-CF_3}$	$C_{11}F_3^+$ at 138.5 mu
$AsC_6F_4^+$	$\xrightarrow{-C_6F_2}$	AsF_2^+ at 57.3 mu
$AsC_6F_4^+$	$\xrightarrow{-AsF_2}$	$C_6F_2^+$ at 54.3 mu
$AsC_6F_4^+$	$\xrightarrow{-AsF_3}$	C_6F^+ at 37.1 mu (?)

Many background peaks are also present due to the fluorocarbon ions $C_6F_a^+ (a, 0 \rightarrow 4)$, $C_5F_b^+ (b, 0 \rightarrow 3)$, $C_{11}F_x^+ (x, 0 \rightarrow 7)$ and $C_{12}F_y^+ (y, 0 \rightarrow 8)$; weak peaks were also noted for $(M-F)^+$, $(M-2F)^+$, $(M-CF_2)^+$ and $(M-CF_3)^+$. Figure 2 shows the mass spectrum of $SbP(C_6F_4)_3$, which is typical of a mixed 1,6-disubstituted triptycene.

Attempts to make the triptycene derivative $Sb(CH_3Si)(C_6F_4)_3$ resulted in a mixture which gave rise to the molecular ions shown in Fig. 3.

The identity of the peaks was confirmed by high-resolution mass measurements on the ions, in particular for the peak cluster around 608 mass units:

$CH_3Si\,^{121}SbC_{18}F_{12}$	607.882 (calcd 607.879)
$CH_3Si\,^{121}Sb\,^{12}C_{17}\,^{13}CF_{12}$	608.886 (calcd 608.883)
$CH_3Si\,^{123}SbC_{18}F_{12}$	609.890 (calcd 609.895)
$CH_3Si\,^{123}Sb\,^{12}C_{17}\,^{13}CF_{12}$	610.887 (calcd 610.886)

Although confirming the presence of the mixed triptycene $Sb(CH_3Si)(C_6F_4)_3$, this partial mass spectrum shows that exchange reactions are occurring during its attempted synthesis (Scheme 1).

A comparison has been made of the triptycene mass spectra recorded under both electron impact (EI) and fast atom bombardment (FAB) conditions, sulpholane being used as the solvent in the latter studies. The fragmentation processes are relatively simple in both types of spectra for $MM'(C_6F_4)_3$ where $M = M'$ or $M \neq M'$; three main ions are observed: parent (P^+), $MM'(C_6F_4)_2^+$ and $MC_6F_4^+$ (also $M'C_6F_4^+$ if $M \neq M'$). The molecular ion is observed in good abundance for all the triptycenes and there does not appear to be a favourable technique for providing the P^+ ion: sometimes FAB gives the more abundant molecular ion ($M = M' =$ As or CH_3Si, and $M = P$, $M' = Sb$) and sometimes electron impact ($M = M' = Sb$ or Bi, and $M = As$, $M' = Sb$). Fluorine migration to the 'metal' atoms of $MM'(C_6F_4)_3$ is amlost completely absent and occurs only in FAB spectra for the cases where $M = M' = As$ and $M = Sb$, $M' =$ As or P. Fluorine radical loss from the molecular ion is also unimportant, whereas fluorine migration to the metal atom followed by loss of MF or MF_2 is much more common; the mixed species show that these metal fluoride losses occur more readily for antimony than either phosphorus or arsenic.

The parent ion can lose one C_6F_4 ring to give **I** but loss of a ring plus a metal atom is more favoured, yielding **II** (Scheme 2). Formation of **II** actually occurs as part of a series of steps (Scheme 3).

The mixed triptycenes show that there is a preference in the first of these steps in that

$$MM'(C_6F_4)_3^+ \rightarrow M'(C_6F_4)^+ + M(C_6F_4)_2$$

occurs for both $M = P$, $M' = Sb$ and $M = As$, $M' = Sb$, the single ring being retained by the antimony. Table 1 summarizes the FAB and EI spectra.

In Table 2 we show the comparison of the fragmentations observed by MIKES and CA MIKES for positive-ion EI, positive-ion FAB and negative-ion FAB. Interestingly, the ions in the positive ion FAB

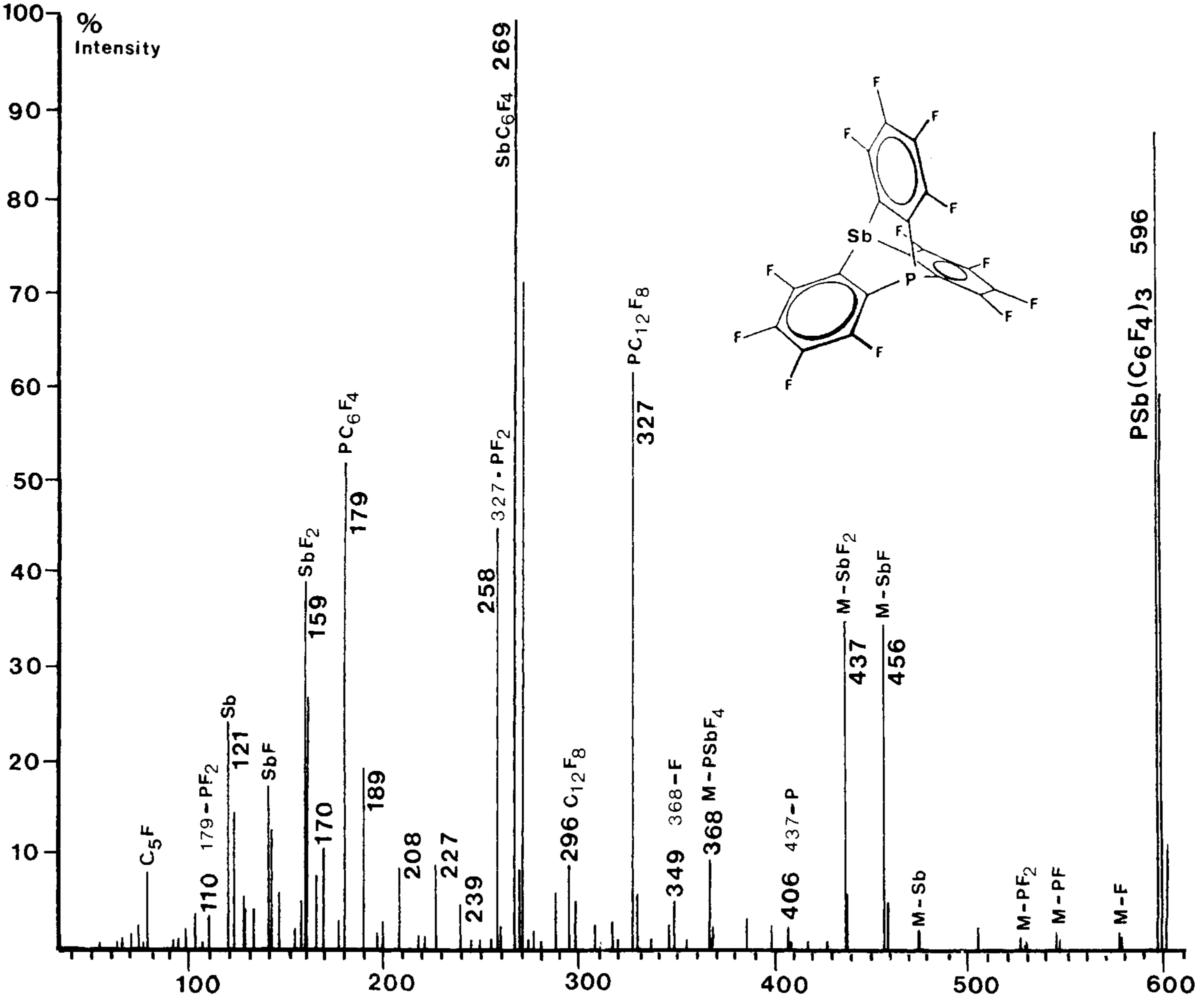
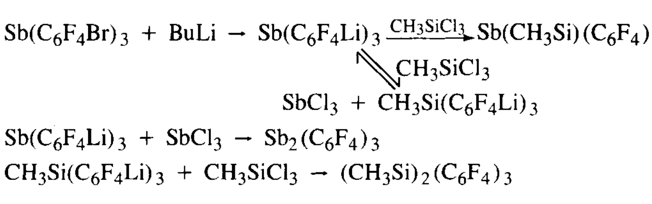


Figure 2 Mass spectrum of the mixed triptycene $SbP(C_6F_4)_3$.



$$Sb(C_6F_4Br)_3 + BuLi \rightarrow Sb(C_6F_4Li)_3 \xrightarrow{CH_3SiCl_3} Sb(CH_3Si)(C_6F_4)_3$$

$$\searrow CH_3SiCl_3$$

$$SbCl_3 + CH_3Si(C_6F_4Li)_3$$

$$Sb(C_6F_4Li)_3 + SbCl_3 \rightarrow Sb_2(C_6F_4)_3$$

$$CH_3Si(C_6F_4Li)_3 + CH_3SiCl_3 \rightarrow (CH_3Si)_2(C_6F_4)_3$$

Scheme 1

spectra are much less prone to fragment, even under CA conditions, than are those in the corresponding EI spectra. However, the ions produced in the negative-ion FAB spectra are much less stable than those observed in the positive-ion mode and fragment almost identially to those in the positive-ion EI spectra.

NMR

The ^{19}F-NMR spectrum of $Sb_2(C_6F_4)_3$ is typical of an AA′XX′ system and, assuming that there is no inter-ring fluorine–fluorine (F–F) coupling, the coupling constants can be derived as $J_{AA'} = +15.4$ Hz,

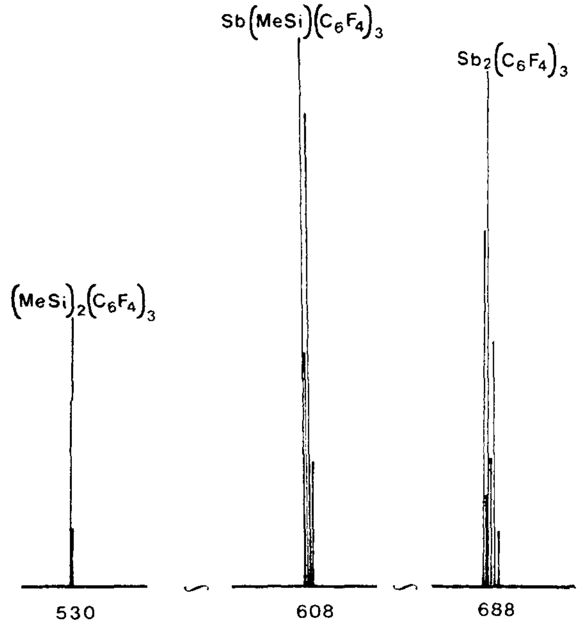
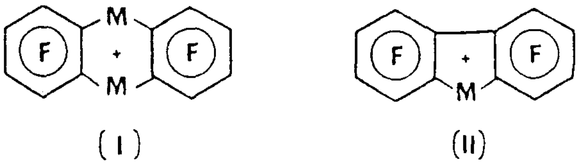
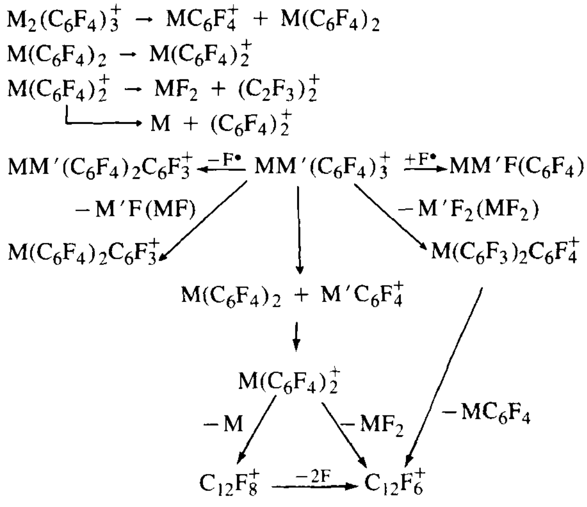


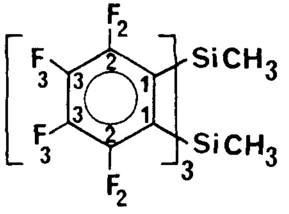
Figure 3 Mass spectrum of mixture resulting from attempts to make $Sb(CH_3Si)(C_6F_4)_3$.



Scheme 2



Scheme 3



Scheme 4

$J_{XX'} = -17.5$ Hz, $J_{AX} = -22.2$ Hz and $J_{AX'} = +5.0$ Hz. When the spectrum is computed using these values there is a very close fit between the observed and the theoretical spectrum as shown in Fig. 4. In the spectrum of $Bi_2(C_6F_4)_3$ peaks 5 and 6 (7 and 8) appear to overlap and occur as a shoulder on peak 1,2 (or 3,4).

In the proton-decoupled ^{13}C NMR spectrum of $(CH_3Si)_2(C_6F_4)_3$ the methyl–carbon resonance is split into a symmetrical septet (Fig. 5) due to $^{13}C-^{19}F$ coupling arising from the six F_2 fluorines (Scheme 4).

Because of the high symmetry of the triptycene skeleton these fluorines act as a six-particle set, the observed splitting (*ca* 2.5 Hz) being the mean value of the individual coupling constants of the two components of the set (i.e. an A_3A_3' X system in which $J_{A'-X} \cong 0$). Hence the A–X coupling is equal to half the observed splitting in the spectrum.

The mixed triptycenes show the expected four resonances in their ^{19}F NMR spectra. When phosphorus is one of the heteroatoms, phosphorus–fluorine coupling splits the resonance due to the fluorine *ortho* to phosphorus into a doublet. As shown in Fig. 6, one-half of this doublet lies under the other *ortho*-fluorine resonance in the ^{19}F NMR spectrum of $PAs(C_6F_4)_3$, J_{P-F} being 110.9 Hz.

Partly due to solvate formation[3] we have had difficulty in growing single crystals of the triptycenes for X-ray structural studies. However, after very considerable effort we were eventually able to obtain suitable crystals of $As_2(C_6F_4)_3$ by subliming samples in open tubes held in an oven at about 100°C for several weeks. A crystal measuring 0.48 mm × 0.41 mm × 0.31 mm was sealed in a Lindemann glass capillary and mounted about *c* on a Stoe Stadi-2 two-circle diffractometer; 2275 reflections were measured of which 1724 had $I > 3\sigma(I)$. A standard reflection was checked every 50 reflections and no significant changes were noted; absorption corrections were applied, $t_{min} = 0.21$ and

Table 1 Partial positive-ion FAB and EI mass spectra of $MM'(C_6F_4)_3$ complexes

	Relative intensity													
M/M' =	P/P		As/As		Sb/Sb		Bi/Bi		CH_3Si/CH_3Si		P/Sb		As/Sb	
	EI	FAB	EI	FAB	EI	FAB	EI	FAB	EI	FAB	EI	FAB	EI	FAB
Metal-containing ions														
$P^{+\cdot}$	19.9		13.3	24.9	9.5	5.3	18.4	3.5	9.7	16.4	21.0	23.8	11.2	9.9
$(P+F)^+$			1.3									1.4		1.6
$(P-F)^+$	1.3		0.1	1.5						1.0	0.6	1.8	0.1	0.8
$(P-MF)^+$	0.8		0.1				0.4		1.4		0.6	0.1	0.1	0.3
$(P-MF_2)^+$	1.1		0.6		0.3		0.4		4.1				0.1	0.2
$(P-M'F)^+$											4.7	0.8	0.1	0.5
$(P-M'F_2)^+$											7.4	1.1	0.8	0.5
$MM'(C_6F_4)_2^{+}$				6.0			0.1	1.8	0.9	0.8		2.1		2.0
$MM'(C_6F_4)_2^{+}+F)^+$								2.2						1.4
$MM'(C_6F_4)_2^{+}-F)^+$				0.2		1.1			2.5			0.5		0.5
$M(C_6F_4)_2^{+}$	5.0		8.2	19.8	5.4	4.3	5.3	1.2		1.9	4.7	4.8	5.7	8.9
$M(C_6F_4)_2^{+}-F)^+$			0.1	7.8				0.7		0.8	0.2	2.1	0.5	2.6
$M'(C_6F_4)_2^{+}$											0.6	1.0	2.1	1.7
$M'(C_6F_4)_2^{+}-F)^+$											0.3	0.4		0.9
$M(C_6F_4)^+$	45.4		54.9	9.9	20.6	18.2	5.3	1.2		0.8	0.3	4.8	18.9	3.5
$M'(C_6F_4)^+$											23.7	3.6	29.1	6.1
MF^+	0.1		0.1	0.7	1.4	1.5	0.6	0.5					0.1	0.3
MF_2^{+}	4.7		2.2	0.9	2.1	3.0	0.1		4.9		1.7		1.1	0.3
$M'F^+$											2,4	0.9	0.7	1.0
$M'F_2^{+}$											4.4		2.2	
M^+	–		–	–	2.9	3.3	47.7	20.9	–	–				
M'^+											2.4		1.3	
Non-metal containing ions														
$C_{18}F_{12}^{+}$			0.3	4.9			0.2			1.3		0.1	0.2	0.3
$C_{12}F_8^{+}$	0.4		1.3		0.9	0.6	0.3		0.3		0.5		1.4	
$C_{12}F_6^{+}$	2.5		3.9	1.0	3.1	3.1	0.3		0.3		3.6	0.3	4.5	1.1
$C_6F_4^{+}$	0.2		0.1		0.5	0.5	0.6	1.1			0.1		0.1	
Other ions														
$(P-CH_3)^+$									10.3	2.6				
$(MM'(C_6F_4)_2-CH_3)^+$									0.4					

Table 2 MIKES, CA-MIKES and normal metastable ion transitions occurring in the mass spectrum of dodecafluorodistibatriptycene, $Sb_2(C_6F_4)_3$[a]

Reaction[b]	Positive EI			Positive FAB		Negative FAB	
	m*	MIKES	CA MIKES	MIKES	CA MIKES	MIKES	CA MIKES
$Sb_2(C_6F_4)_3^{+\cdot} \rightarrow Sb_2(C_6F_4)_2C_6F_3^{+} + F^{\cdot}$	–	–	–	√	√	√	√
$Sb_2(C_6F_4)_3^{+\cdot} \rightarrow Sb(C_6F_3)_2C_6F_4^{+} + SbF_2^{\cdot}$	–	√	√	–	–	√	√
$Sb_2(C_6F_4)_3^{+\cdot} \rightarrow Sb(C_6F_3)_3^{+\cdot} + SbF_3$	–	√	√	–	–	√	√
$Sb_2(C_6F_4)_3^{+\cdot} \rightarrow Sb(C_{18}F_8)^{+} + SbF_4^{\cdot}$	–	√	√	–	–	–	–
$Sb_2(C_6F_4)_3^{+\cdot} \rightarrow Sb(C_6F_4)_2^{+} + SbC_6F_4^{\cdot}$	–	√	√	–	–	√	√
$Sb_2(C_6F_4)_3^{+\cdot} \rightarrow Sb(C_{12}F_7)^{+\cdot} + FSbC_6F_4$	–	–	–	–	–	√	√
$Sb_2(C_6F_4)_3^{+\cdot} \rightarrow SbC_6F_4^{+} + SbC_6F_4)_2^{\cdot}$	√	√	√	–	–	–	–
$Sb(C_{18}F_{10})^{+} \rightarrow C_{18}F_{10}^{+\cdot} + Sb^{\cdot}$	√	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
$Sb(C_{18}F_{10})^{+} \rightarrow C_{18}F_8^{+\cdot} + SbF_2^{\cdot}$	√	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
$Sb(C_6F_4)_2^{+} \rightarrow Sb(C_6F_4)(C_6F_3)^{+} + F^{\cdot}$	–	–	–	–	–	√	–
$Sb(C_6F_4)_2^{+} \rightarrow C_{12}F_8^{+\cdot} + Sb^{\cdot}$	√	√	√	–	–	√	√
$Sb(C_6F_4)_2^{+} \rightarrow C_{12}F_7^{+} + SbF$	–	–	–	–	–	√	√
$Sb(C_6F_4)_2^{+} \rightarrow C_{12}F_6^{+\cdot} + SbF_2^{\cdot}$	√(str)	–	√	–	–	√(wk)	–
$Sb(C_6F_4)_2^{+} \rightarrow C_{12}F_5^{+} + SbF_3$	–	√	–	–	–	√	√
$Sb(C_6F_4)^{+} \rightarrow SbC_6F_3^{+\cdot} + F^{\cdot}$	–	–	√	–	√	Parent not observed	
$Sb(C_6F_4)^{+} \rightarrow SbC_6F_2^{+} + F_2$	√	–	√	–	√	Parent not observed	
$Sb(C_6F_4)^{+} \rightarrow SbC_5F^{+\cdot} + CF_3^{\cdot}$	–	–	–	–	√	Parent not observed	
$Sb(C_6F_4)^{+} \rightarrow SbF_2^{+} + C_6F_2$	√	√	√	–	–	Parent not observed	
$Sb(C_6F_4)^{+} \rightarrow SbF^{+\cdot} + C_6F_3^{\cdot}$	–	–	√	–	–	Parent not observed	
$Sb(C_6F_4)^{+} \rightarrow Sb^{+} + C_6F_4$	√	√	√	–	–	Parent not observed.	

[a] √ shows the presence of the designated reaction. Abbreviations: MIKES, mass-analysed ion kinetic energy spectrometry; CA MIKES, collisional activation MIKES; m*, metastable ion; n.d., not determined; str, strong; wk, weak. [b] Negative ions as parents and products in the case of the negative-ion FAB data.

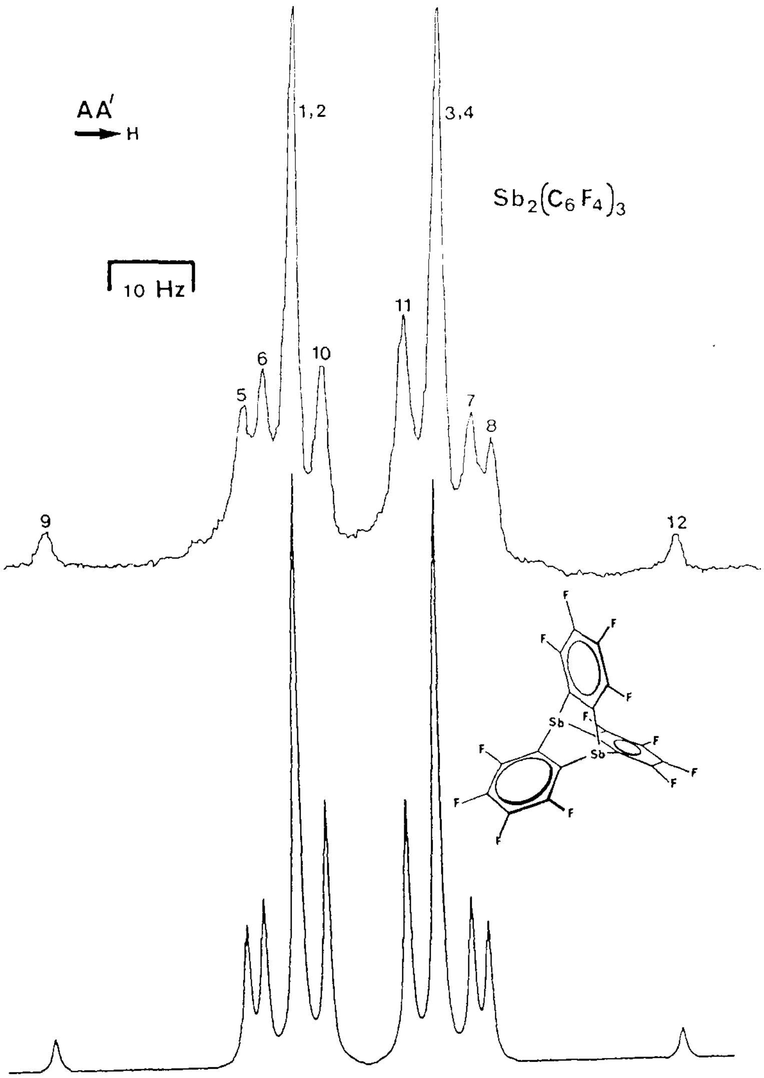


Figure 4 The observed and theoretical AA' part of the ^{19}F NMR spectrum of $Sb_2(C_6F_4)_3$.

$r_{max} = 0.37$. The two arsenics were located by direct methods, and the carbon and fluorine atoms from successive ΔF syntheses; anisotropic refinement gave a final $R = 0.025$, $\Delta/\sigma < 0.2$ and $\Delta\rho$ excursions = +0.29 to −0.31 e Å^{-3}. A copy of the list of structure factors and anisotropic temperature factors is available on request from one of the authors (JBJ).

Crystal data

$C_{18}F_{12}As_2$, $M_r = 594.022$, monoclinic Cc, $a = 16.606(3)$ Å, $b = 8.824(3)$ Å, $c = 14.98(3)$ Å, $\beta = 124.94(2)°$, $U = 1799.75$ Å^3, $Z = 4$, $D_m = 2.159$ g cm^{-3}, $D_x = 2.192$ g cm^{-3}, $\lambda(MoK\alpha) = 0.71069$ Å, $\mu = 39.88$ cm^{-1}, $F(000) = 1128$, $T = 293$ K, final $R = 0.025$ for 1724 observed reflections with $I > 3\sigma(I)$.

An ORTEP[5] diagram of the molecule is shown in Fig. 7, with a **b**-projection of the contents of the unit cell in Fig. 8; the diffraction results thus confirm the triptycene-like structure of dodecafluoro-1,6-diarsatriptycene [$As_2(C_6F_4)_3$], the sample having been made by direct synthesis. The aromatic rings are essentially planar, the dihedral angles between the ring-planes being 111(2)°, 125(2)° and 125(2)°. Similar alternations in dihedral angles have been noted[6] in

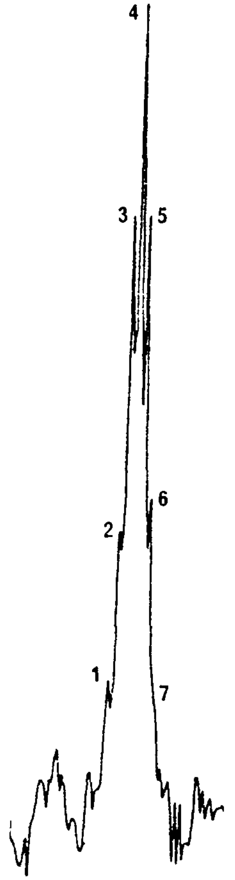


Figure 5 The ^{13}C resonance of the methyl carbon atom in $(CH_3Si)_2(C_6F_4)_3$ after the accumulation of 94 000 scans.

some hydrogen-substituted triptycenes where the lack of the expected high symmetry was assumed to be due to crystal forces. Although models depict triptycenes as totally rigid systems, in fact the molecules appear to behave as three rigid benzenoid rings flexibly connected to the bridgehead atoms.[7] Mean aromatic ring bond lengths and angles are 1.383(13) Å and 119.9(9)° respectively and the mean C—As length is 1.969(10) Å.

EXPERIMENTAL

The preparation of the fully fluorinated 1,6-disubstituted triptycenes has been described previously.[2,3]

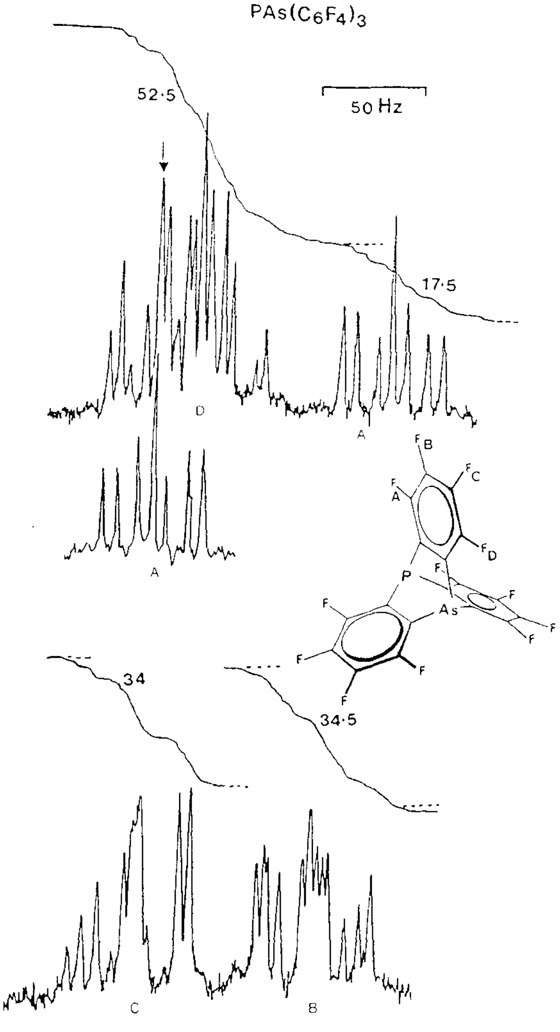


Figure 6 ^{19}F NMR spectrum of $PAs(C_6F_4)_3$.

Reaction of 1,2-di-iodotetrafluorobenzene ($1,2\text{-}I_2C_6F_4$) with arsenic–arsenic(III) oxide ($As\text{–}As_2O_3$) mixtures

There was no reaction between 1,2-di-iodotetrafluorobenzene and arsenic(III) oxide (As_2O_3) at 300°C in a sealed, evacuated tube; however, when arsenic (ca. 10 mmol) was added (2:1:1 mole ratio) to the mixture, arsenic(III) iodide (AsI_3) was rapidly formed. Most of the tri-iodide was removed by dissolving the other products in 60—80°C petrol ether; the remaining AsI_3 was destroyed by washing the petrol solution with dilute sodium hydroxide (NaOH) and sodium thiosulphate ($Na_2S_2O_3$). After separation from the aqueous phase the petroleum ether was boiled

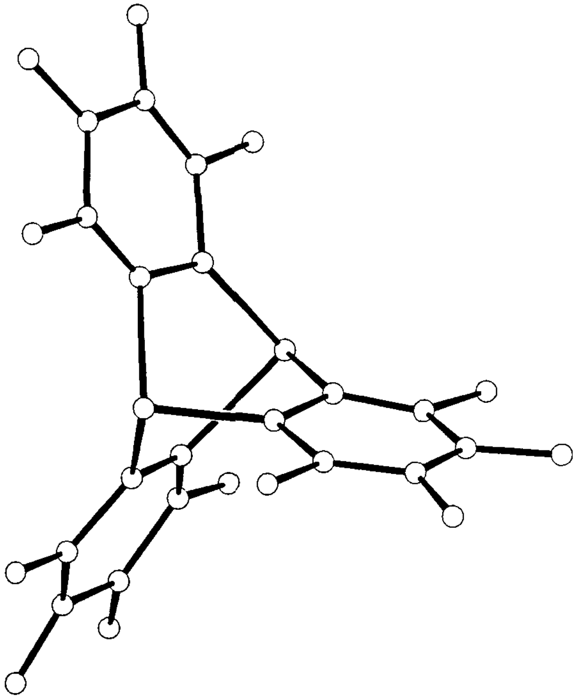


Figure 7 ORTEP diagram of the $As_2(C_6F_4)_3$ molecule.

with charcoal, filtered and evaporated down to allow crystallization. Two major components were present in the crystalline mass and were separated by preparative-scale thin-layer chromatography on alumina. The faster-running component was shown to be $As_2(C_6F_4)_3$ by comparison of its infrared spectrum with that of an authentic sample. The other product was the epoxide, $OAs_2(C_6F_4)_2$ (Found: C, 31.2; F, 33.1. $C_{12}F_8As_2O$ calcd: C, 31.2; F, 32.9%). An accurate mass determination on the parent ion in the mass spectrum gave 461.825 (calcd for $^{12}C_{12}F_8As_2O$, 461.830) and 462.829 (calcd for $^{12}C_{11}{}^{13}CF_8As_2O$, 462.833). The epoxide separates from petrol as rosettes of crystals having m.p. 148 °C.

Reaction of chlorine $(Cl)_2$ with $As_2(C_6F_4)_3$

A solution of $As_2(C_6F_4)_3$ in carbon tetrachloride was held at room temperature while chlorine gas was bubbled through. Little turbidity was apparent until water was added, when a white precipitate rapidly formed. This solid was recrystallized from carbon tetrachloride; elemental analysis indicated a hemisolvate was formed (Found: C, 30.8; H, 0.2; F, 31.6. $(AsO)_2(C_6F_4)_3.0.5CCl_4$ calcd: C, 31.6; H, 0.2; F, 32.4%). The mass spectrum confirmed the presence of copious amounts of CCl_x^+ ions and the parent ions had accurate masses of 625.819 (calcd for $^{12}C_{18}F_{12}As_2O_2$, 625.823) and 626.824 (calcd for $^{12}C_{17}{}^{13}CF_{12}As_2O_2$, 626.826).

Other reactions of $As_2(C_6F_4)_3$

A sample of $As_2(C_6F_4)_3$ was recovered unchanged after being boiled with concentrated nitric acid for 5 min. The melting point and infrared spectra of $As_2(C_6F_4)_3$ samples refluxed with methyl iodide

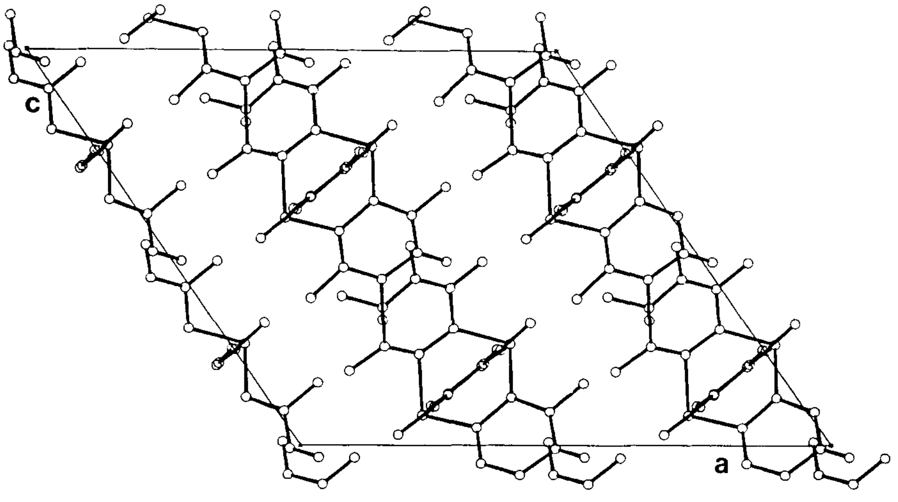


Figure 8 Contents of the $As_2(C_6F_4)_3$ unit cell projected down the **b** axis.

and with iodine–carbon tetrachloride–water (I_2–CCl_4–H_2O) mixtures remained unchanged after treatment indicating there was no detectable reaction; the latter experiment was carried out in an effort to make the epoxide $OAs_2(C_6F_4)_2$ via degradation.

Direct synthesis and some reactions of $Bi_2(C_6F_4)_3$

Previously, attempts at direct syntheses of $Bi_2(C_6F_4)_3$ using granular bismuth and 1,2-di-*iodotetrafluoro*benzene (1,2-$I_2C_6F_4$) had given only polyfluorophenylene derivatives, $(C_6F_4)_x$. However, when finely powdered bismuth is heated in a sealed, evacuated tube with 1,2-di-iodotetrafluorobenzene, yields of $Bi_2(C_6F_4)_3$ approaching 20% can be achieved. The product is extracted from the broken tube using hexane; the solution is then boiled with charcoal and evaporated down to crystallize. The melting point is of the bismuth derivative 318°C and partial sublimation occurs below this temperature to give needle-shaped crystals on the cool parts of the melting-point tube. (Found: C, 25.3; F, 26.1. $C_{18}F_{12}Bi_2$ calcd: C, 25.1; F, 26.4%.) This analytical sample had been heated in an oven for 12 h at 90°C to drive off the solvent. Analyses of samples which had not been heated showed the presence of 'hydrogen' due to solvate formation. The hexane hemi-solvate is rather unstable and loses hexane on standing at room temperature; gravimetric analysis showed a 12.8% loss of hexane at 20°C in 12 h. The cyclohexane hemi-solvate was more stable but gave a poor carbon analysis (C, 28.9, 28.7; H, 0.7, 0.6; F, 25.4. $C_{18}F_{12}Bi_2 . 0.5C_6H_{12}$ calcd: C, 27.9; H, 0.7; F, 25.2%).

When $Bi_2(C_6F_4)_3$ was dissolved in carbon tetrachloride (CCl_4), treated with chlorine (Cl_2) at room temperature and water added to the mixture, only bismuth oxychloride (BiOCl) could be identified in the precipitated white solid. From this it would appear that tetrafluorophenyl (C_6F_4) groups have been cleaved from the bismuth to give bismuth trichloride ($BiCl_3$) and that this hydrolysed to give a precipitate of bismuth oxychloride (BiOCl) on addition of water.

There was no reaction with $Bi_2(C_6F_4)_3$ was refluxed with iodine in carbon tetrachloride (CCl_4). Similarly, no reaction occurred when $Bi_2(C_6F_4)_3$ was boiled with water containing a small amount of alcohol (used to wet the water-insoluble solid).

Mass spectral studies

Positive-ion electron impact (EI) spectra were obtained on both a Kratos MS80 (at Loughborough, UK) and an AEI MS30 (4 keV, Kratos DS-55 Data System – Brock, Canada), at a nominal 1000 resolving power. Positive-ion fast atom bombardment (FAB) spectra were obtained on the MS-30 with a Kratos FAB source retrofit. The MIKES and CA MIKES spectra, both EI and positive and negative FAB, were obtained on the VG ZAB-E instrument (8 keV) at the regional mass spectrometer facility, McMaster University, Hamilton, Ontario, Canada.

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