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Pentafluorophenylarsines. The crystal and molecular structures of tetrakis(pentafluorophenyl)diarsine, $(C_6F_5)_2AsAs(C_6F_5)_2$, tetrakis(pentafluorophenyl)diarsenic(III) oxide, $(C_6F_5)_2AsOAs(C_6F_5)_2$, and tris(pentafluorophenyl)arsine *

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Abstract

Crystalline materials from a high-boiling fraction obtained as by-products in the preparation of $C_6F_5AsCl_2$, or from subsequent reaction with elemental mercury, have been crystallographically identified as consisting primarily of secondary and tertiary substituted pentafluorophenylarsenic compounds. The crystal and molecular structures of three of these products are reported: $(C_6F_5)_2AsAs(C_6F_5)_2$ (**1**), $(C_6F_5)_2AsOAs(C_6F_5)_2$ (**2**), and $(C_6F_5)_3As$ (**3**). **1**: $C_{24}F_{20}As_2$, tetragonal, $P\bar{4}2_1c$, *a* 13.253(3), *c* 42.584(10) Å, *V* 7479 Å^3, $Z = 12$ (three independent half-molecules), $R(F)$ 6.54%. **2**: $C_{24}F_{20}As_2O$, monoclinic, $C2/c$, *a* 16.676(5), *b* 7.755(2), *c* 22.266(6) Å, β 117.13(2)°, *V* 2563 Å^3, $Z = 4$ (one half-molecule), $R(F)$ 4.85%. **3**: $C_{18}F_{15}As$, triclinic, $P\bar{1}$, *a* 8.902(2), *b* 10.888(2), *c* 11.185(2) Å, α 109.59(2), β 103.12(2), γ 106.95°, *V* 911.3(4) Å^3, $R(F)$ 4.50%. **1** is twisted 16.5° from a *trans* conformation and contains the longest As–As bond reported for any organoarsenic compound, 2.479(4) Å. However, non-bonded F...F contact distances fail to support steric reasons for these distortions. **2** has an As–O–As angle of 116.2(3)° determined primarily by lattice packing effects. **3** is pyramidal with As–C distances and C–As–C angles typical of triarylarsines.

Introduction

In the course of our study of the reactions of metal carbonyls with cyclopoly(organoarsines), cyclo-$(RAs)_n$, we have investigated systems with $R = C_6F_5$, specifically, cyclo-$(C_6F_5As)_4$ [1]. The preparative steps leading to this cyclotetraar-

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* Dedicated to the memory of Jerry Zuckerman whose love of inorganic chemistry and its workers made ours a happier profession.

sine [2] are accompanied by substantial scrambling of substituents in its primary arsine precursors. In turn, this led to the isolation and characterization of several secondary and tertiary substituted by-products. We now report the crystal and molecular structures of three of these by-products: tetrakis(pentafluorophenyl)diarsine, $(C_6F_5)_2AsAs(C_6F_5)_2$ (**1**), tetrakis(pentafluorophenyl)diarsenic(III) oxide, $(C_6F_5)_2AsOAs(C_6F_5)_2$ (**2**), and tris(pentafluorophenyl)arsine, $(C_6F_5)_3As$ (**3**).

Surprisingly few mono- and di-arsenic structures have been previously reported. **1** is the first tetraaryldiarsine and only the second in which the substituents at As are not contained in a heterocycle [3a,b *] to be structurally characterized, **2** is the second diarsenic oxide characterized, and, **3** is only the fourth structure of an uncoordinated tertiary arsine to be reported [3c *]. In general pentafluorophenyl-substituted arsenic compounds have not been well studied despite a well developed coordination chemistry of tris(pentafluorophenyl)phosphine. An $Fe(CO)_4$ complex of the diarsene, $C_6F_5AsAsC_6F_5$, has been crystallographically confirmed as containing a three-membered As_2Fe ring [4].

Experimental

Preparation of 1, 2, and 3

Following the method of Green and Kirkpatrick [2] for the preparation of $C_6F_5AsCl_2$, a high boiling fraction (~ 10%, b.p. 110–140 °/6 mmHg) was obtained as a minor component which was found to be substantially the disubstituted product $(C_6F_5)_2AsCl$ with a small quantity ($< 1\%$) of the trisubstituted product, $(C_6F_5)_3As$. This fraction (1.85 g, 26.7 mmol) was shaken with 20 ml Hg^0 at 100 ° C under N_2 for 3 h. The solid mass formed was twice extracted with 125 ml of hot (100 ° C) toluene. Evaporation of the toluene at room temperature left a yellow oil which produced a white solid on crystallization from toluene/hexane. The majority of the product was **1**, but microscopic examination of the product revealed the presence of small quantities of materials distinctly different from the tetragonal habit of **1**; these were identified by single-crystal X-ray diffraction as **2** and **3**, in addition to a fourth product, $C_6F_5As(O)(OH)_2$, whose structure will be reported separately. **1** sublimes readily at room temperature and 1 atm; consequently, crystallographic samples must be made fresh and immediately encapsulated to prevent loss. High yield procedures to **1**, **2** and **3** are available [2].

Crystallographic structure determination

Colorless crystals of **1**, **2**, and **3** were mounted on glass fibers with epoxy resin. Unit-cell parameters were determined by least-squares refinement of the angular settings for 25 reflections each ($20° \leqslant 2\theta \leqslant 25°$). Data were collected using a Nicolet R3m/μ diffractometer with a graphite monochromator and Mo-K_α radiation. Empirical absorption corrections (6 reflections, ψ scan, 216 data) were applied to the data for all structures. Crystal data for **1**, **2** and **3** are collected in Table 1.

Solution and structure refinement

The structures were solved by direct methods which located the As atoms. Locations of the remaining atoms were determined through subsequent Fourier

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* Reference number with asterisk indicates note in the list of references.

Table 1

Crystal parameters for **1**, **2** and **3**

	1	**2**	**3**
Structure	$C_{24}F_{20}As_2$	$C_{24}F_{20}As_2O$	$C_{18}F_{15}As$
M.W.	818.07	834.07	576.10
Cryst. syst.	tetragonal	monoclinic	triclinic
Space group	$P\bar{4}2_1c$	$C2/c$	$P\bar{1}$
a, Å	13.253(3)	16.676(5)	8.902(2)
b, Å	13.253(3)	7.755(2)	10.888(2)
c, Å	42.584(10)	22.266(6)	11.185(2)
α, deg	90	90	109.59(2)
β, deg	90	117.13(2)	103.12(2)
γ, deg	90	90	106.95(2)
V, Å^3	7479(3)	2563(1)	911.3(4)
Z	12	4	2
T, K	296	296	293
D(calc), g cm^{-3}	2.18	2.16	2.10
μ(Mo-K_α), cm^{-1}	30.1	29.4	21.4
Crystal size, mm	$0.35 \times 0.35 \times 0.35$	$0.16 \times 0.32 \times 0.40$	$0.36 \times 0.38 \times 0.39$
hkl collected	$+15, +15, +46$	$\pm 20, +10, +27$	$\pm 13, \pm 14, +15$
Scan type	ω	Wyckoff	Wyckoff
2θ limits, deg	4–45	4–50	4–60
Reflns. collected	6903	2496	4566
Independent refns (R_{int}, %)	3654(0)	2252(1.3)	4349(0.9)
Observed reflns ($F_0 \geq 5\sigma$)	1866	1738	2967
L.S. parameters	371	213	308
$R(F)$, %	6.54	4.85	4.50
$R(wF)$, %	5.78	4.67	4.63
GOF	1.197	1.159	1.106
Δ/σ max	0.022	0.065	0.050
$\Delta(\rho)$ max e Å^{-3}	0.71	0.42	0.47

analyses and least-squares refinement. All atoms in **2** and **3** were anisotropically refined, while in **1**, to conserve data, only non-carbon atoms were refined anisotropically. Additionally, the phenyl rings in **1** were constrained to rigid, planar hexagons with d(C–C) 1.38 Å, the average value found in **3**. Systematic absences of reflections uniquely determined the space group $P\bar{4}2_1c$ for **1**. Systematic absences for **2** determined the possible space groups $C2/c$ and Cc. $C2/c$ was suggested by the distribution of E-values and confirmed by the chemically sensible results of refinement. The correct, centrosymmetric space group for **3** was similarly determined. Tables 2, 3 and 4 contain atom coordinates for **1**, **2** and **3**, respectively, and Tables 5, 6, and 7 list selected bond lengths and angles. All calculations used SHELXTL (5.1) software (G. Sheldrick, Nicolet XRD, Madison, WI).

Results and discussion

Tetrakis(pentafluorophenyl)diarsine

$(C_6F_5)_2AsAs(C_6F_5)_2$ (**1**) crystallizes in the tetragonal space group $P\bar{4}2_1c$ with the crystallographic asymmetric unit containing three independent half-molecules; a crystallographic two-fold rotational axis intersects each of the As–As bonds (Fig. 1,

Table 2

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters (Å^2 $\times 10^3$) for 1

	x	y	z	U
As(1)	657(1)	9329(1)	9098(1)	55(1) [a]
As(2)	4253(1)	9440(1)	8423(1)	51(1) [a]
As(3)	9398(2)	5714(2)	8792(1)	59(1) [a]
C(11)	2602(8)	9359(7)	9380(2)	59(5)
C(12)	3344	9562	9604	64(5)
C(13)	3147	10238	9847	61(5)
C(14)	2210	10712	9867	52(4)
C(15)	1468	10509	9643	53(5)
C(16)	1664	9833	9400	46(4)
F(11)	2815(7)	8762(7)	9145(2)	72(4) [a]
F(12)	4253(7)	9136(9)	9582(2)	85(4) [a]
F(13)	3858(7)	10423(9)	10064(2)	93(5) [a]
F(14)	2023(8)	11316(8)	10107(2)	87(5) [a]
F(15)	575(7)	10946(7)	9677(2)	75(4) [a]
C(21)	1476(9)	10973(8)	8688(2)	51(5)
C(22)	1694	11403	8397	63(5)
C(23)	1661	10814	8125	50(5)
C(24)	1410	9794	8145	58(5)
C(25)	1191	9363	8436	60(5)
C(26)	1224	9952	8708	56(5)
F(21)	1548(9)	11560(7)	8938(2)	75(4) [a]
F(22)	1886(8)	12364(7)	8368(3)	87(5) [a]
F(23)	1846(9)	11224(9)	7848(2)	91(5) [a]
F(24)	1374(10)	9234(10)	7891(3)	126(6) [a]
F(25)	923(9)	8418(8)	8459(3)	102(5) [a]
C(31)	5457(7)	8075(8)	7998(2)	44(4)
C(32)	5611	7571	7714	42(4)
C(33)	4988	7773	7457	60(5)
C(34)	4212	8477	7484	54(5)
C(35)	4057	8981	7768	70(6)
C(36)	4680	8780	8025	53(5)
F(31)	6069(8)	7887(8)	8227(2)	85(5) [a]
F(32)	6356(8)	6906(9)	7681(2)	101(5) [a]
F(33)	5116(10)	7279(9)	7183(2)	94(5) [a]
F(34)	3636(9)	8687(9)	7239(2)	90(5) [a]
F(35)	3359(8)	9681(8)	7778(2)	87(5) [a]
C(41)	5468(8)	8535(6)	8942(3)	52(5)
C(42)	5707	7777	9157	63(5)
C(43)	5199	6855	9146	50(5)
C(44)	4453	6692	8921	60(5)
C(45)	4214	7450	8706	45(4)
C(46)	4722	8371	8717	49(5)
F(41)	5951(8)	9387(7)	8980(2)	80(4) [a]
F(42)	6392(9)	7864(8)	9379(3)	95(5) [a]
F(43)	5424(8)	6113(7)	9346(2)	88(5) [a]
F(44)	3983(8)	5822(7)	8904(2)	84(4) [a]
F(45)	3516(8)	7300(8)	8492(2)	80(4) [a]
C(51)	8568(9)	5994(7)	9410(3)	71(6)
C(52)	7966	5803	9672	67(5)
C(53)	7493	4869	9705	86(7)
C(54)	7621	4127	9476	65(6)
C(55)	8223	4318	9214	66(5)
C(56)	8697	5251	9181	53(5)

Table 2 (continued)

	x	y	z	U
F(51)	8995(9)	6871(8)	9393(2)	93(5) [a]
F(52)	7873(10)	6515(10)	9896(3)	119(6) [a]
F(53)	6928(10)	4672(11)	9956(2)	129(7) [a]
F(54)	7176(9)	3237(10)	9505(2)	101(5) [a]
F(55)	8305(9)	3596(8)	8998(2)	83(4) [a]
C(61)	7411(9)	5598(7)	8528(2)	54(5)
C(62)	6650	5350	8315	57(5)
C(63)	6845	4673	8072	67(6)
C(64)	7801	4243	8042	68(6)
C(65)	8562	4490	8255	65(6)
C(66)	8367	5168	8498	46(5)
F(61)	7186(7)	6222(8)	8754(2)	79(4) [a]
F(62)	5745(7)	5774(8)	8339(2)	91(4) [a]
F(63)	6121(7)	4452(9)	7865(2)	96(5) [a]
F(64)	7966(8)	3595(9)	7810(3)	98(5) [a]
F(65)	9451(7)	4091(9)	8213(2)	88(5) [a]

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[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{Å}^2 \times 10^3$) for **2**

	x	y	z	U [a]
As	9181.6(4)	2015.6(8)	1808.9(2)	39.6(2)
O	10000	795(7)	2500	43(2)
C(1)	8103(4)	1076(8)	2536(3)	48(2)
C(2)	7335(4)	736(7)	2585(3)	50(3)
C(3)	6521(4)	756(8)	2017(4)	57(3)
C(4)	6495(4)	1137(9)	1404(3)	55(3)
C(5)	7271(4)	1452(8)	1372(3)	47(2)
C(6)	8114(3)	1401(7)	1929(3)	41(2)
C(7)	8804(4)	−1456(8)	1179(3)	49(3)
C(8)	8658(4)	−2628(8)	679(3)	60(3)
C(9)	8724(4)	−2094(10)	111(3)	63(3)
C(10)	8956(4)	−431(10)	60(3)	58(3)
C(11)	9090(3)	708(8)	562(3)	48(2)
C(12)	9002(3)	235(7)	1135(2)	39(2)
F(1)	8886(2)	1087(6)	3115(2)	78(2)
F(2)	7370(3)	401(5)	3185(2)	74(2)
F(3)	5767(2)	446(6)	2073(2)	87(2)
F(4)	5695(2)	1179(7)	848(2)	87(2)
F(5)	7234(2)	1858(5)	767(2)	69(2)
F(7)	8718(3)	−2008(5)	1722(2)	74(2)
F(8)	8434(3)	−4267(5)	727(2)	97(3)
F(9)	8584(3)	−3228(6)	−377(2)	103(3)
F(10)	9042(3)	65(6)	−484(2)	83(2)
F(11)	9323(3)	2332(5)	509(2)	65(2)

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[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$) for **3**

	x	y	z	U [a]
As(1)	4544.3(5)	1750.1(4)	3461.3(4)	48.2(2)
F(1)	2419(3)	583(3)	140(3)	73(1)
F(2)	−135(4)	−1893(3)	−1497(3)	89(2)
F(3)	−1122(4)	−3907(3)	−604(3)	98(2)
F(4)	510(4)	−3416(3)	1981(4)	101(2)
F(5)	3113(4)	−916(3)	3651(3)	83(2)
F(11)	5621(3)	−922(3)	2028(3)	81(1)
F(12)	8666(4)	−968(3)	2669(4)	104(2)
F(13)	11364(3)	1361(4)	4581(4)	102(2)
F(14)	10991(3)	3806(3)	5846(3)	102(2)
F(15)	7926(3)	3861(3)	5254(3)	83(1)
F(21)	6210(3)	1807(3)	1172(3)	68(1)
F(22)	7103(4)	3876(3)	361(3)	85(2)
F(23)	6306(4)	6144(3)	1267(3)	100(2)
F(24)	4493(4)	6300(3)	2923(3)	104(2)
F(25)	3602(3)	4231(3)	3751(3)	81(2)
C(1)	2007(5)	−381(4)	639(4)	53(2)
C(2)	680(5)	−1646(5)	−219(4)	61(2)
C(3)	164(5)	−2673(5)	229(5)	67(2)
C(4)	1002(5)	−2422(5)	1528(5)	67(2)
C(5)	2317(5)	−1148(4)	2371(4)	57(2)
C(6)	2881(4)	−70(4)	1977(4)	49(2)
C(11)	6905(5)	259(4)	3000(4)	54(2)
C(12)	8463(5)	225(5)	3304(5)	63(2)
C(13)	9829(5)	1405(5)	4267(5)	67(3)
C(14)	9653(5)	2641(5)	4920(5)	66(2)
C(15)	8082(5)	2640(4)	4590(4)	56(2)
C(16)	6664(4)	1483(4)	3647(4)	47(2)
C(21)	5809(5)	2916(4)	1645(4)	50(2)
C(22)	6265(5)	3967(5)	1213(4)	60(2)
C(23)	5836(6)	5108(4)	1664(4)	66(2)
C(24)	4937(6)	5198(4)	2507(4)	66(2)
C(25)	4496(5)	4135(4)	2929(4)	57(2)
C(26)	4944(5)	2987(4)	2543(4)	47(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

2 and 3). The three independent molecules differ remarkably little in their structures, an indication that the structures are not extensively affected by intermolecular forces. The shortest intermolecular F · · · F contacts do not penetrate van der Waals radii. The geometry at the As atom is pyramidal.

Of primary concern in the structure of **1** is its rotational conformation. Considerable experimental and theoretical attention has been given to the rotameric forms of hydrazines and diphosphines for over half a century [3a,5,6]. Considerably less attention has been given to the heavier group-15 congeners, although the general conclusion has been drawn that, for the structure R_4E_2, the *trans* rotamer is favored by increasing the E–E bond distance and increasing the electronegativity of R [5].

The three molecules of **1** all show nearly the same distortion from a *trans* conformation (see Fig. 2 and Table 5). The two average C–As–As′–C′ torsion

Table 5

Selected bond lengths and angles for $(C_6F_5)_2AsAs(C_6F_5)_2$ (1)

mol. A		mol. B		mol. C	
(a) Bond distances (Å)					
As(1)–As(1a)	2.488(4)	As(2)–As(2a)	2.474(4)	As(3)–As(3a)	2.475(4)
As(1)–C(16)	1.970(10)	As(2)–C(36)	1.990(9)	As(3)–C(56)	1.996(12)
As(1)–C(26)	2.002(9)	As(2)–C(46)	1.990(10)	As(3)–C(66)	1.991(11)
F–C (ave)	1.320(14)	F–C (av)	1.319(14)	F–C (av)	1.322(15)
(b) Bond angles (deg)					
C(16)–As(1)–C(26)	98.5(4)	C(36)–As(2)–C(46)	97.8(4)	C(56)–As(3)–C(66)	95.2(4)
C(16)–As(1)–As(1a)	88.2(3)	C(36)–As(2)–As(2b)	92.1(3)	C(56)–As(3)–As(3c)	93.7(3)
C(26)–As(1)–As(1a)	103.5(3)	C(46)–As(2)–As(2b)	100.2(3)	C(66)–As(3)–As(3c)	99.4(3)
(c) Torsion angles (deg)					
C(16)–As(1)–As(1a)–C(16a)	95.7	C(46)–As(2)–(As(2b)–C(46b)	100.5	C(66)–As(3)–As(3c)–C(66c)	100.7
C(26)–As(1)–As(1a)–C(26a)	67.8	C(36)–As(2)–As(2b)–C(36b)	63.0	C(56)–As(3)–As(3c)–C(56c)	67.5

Table 6

Selected bond lengths and angles for $(C_6F_5)_2AsOAs(C_6F_5)_2$ (**2**)

(a) Bond lengths (Å)			
As–O	1.792(3)	F–C (av)	1.343(7)
As–C(6)	1.976(6)	C–C (av)	1.373(9)
As–C(12)	1.959(5)	As...As(a)	3.043(1)
(b) Bond angles (deg)			
As–O–As(a)	116.2(3)	As–C(6)–C(5)	118.6(5)
C(6)–As–C(12)	95.8(2)	As–C(12)–C(7)	125.4(5)
O–As–C(6)	97.8(2)	As–C(12)–C(11)	118.1(4)
O–As–C(12)	94.4(2)	C–C–F (av)	119.6(6)
As–C(6)–C(1)	126.2(3)	C–C–C (av)	120.0(6)

Table 7

Selected bond distances and angles for $(C_6F_5)_3As$ (**3**)

(a) Bond distances (Å)			
As(1)–C(6)	1.960(3)	F–C (av)	1.341(6)
As(1)–C(16)	1.967(4)	C–C (av)	1.376(7)
As(1)–C(26)	1.952(5)		
(b) Bond angles (deg)			
C(6)–As(1)–C(16)	102.6(2)	C(16)–As(1)–C(26)	96.2(2)
C(6)–As(1)–C(26)	102.8(2)		

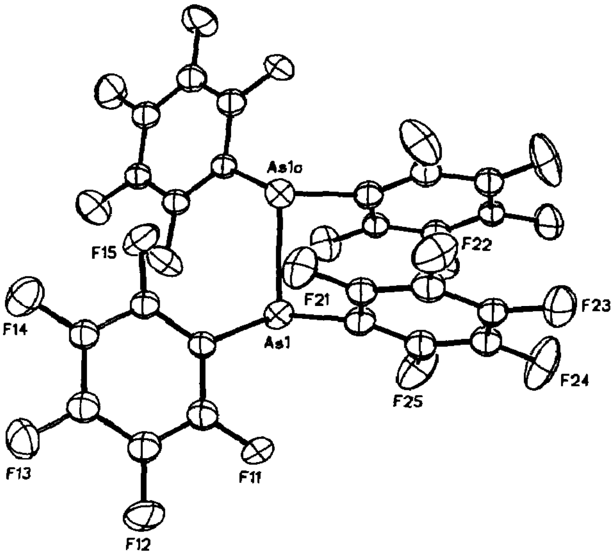

Fig. 1. Molecular structure and numbering scheme for $(C_6F_5)_2AsAs(C_6F_5)_2$ (**1**); the C and F atoms have the same numbers. One of three crystallographically independent, but chemically similar, molecules is shown. A two-fold axis bisects the As–As(a) bond and lies approximately in the paper plane.

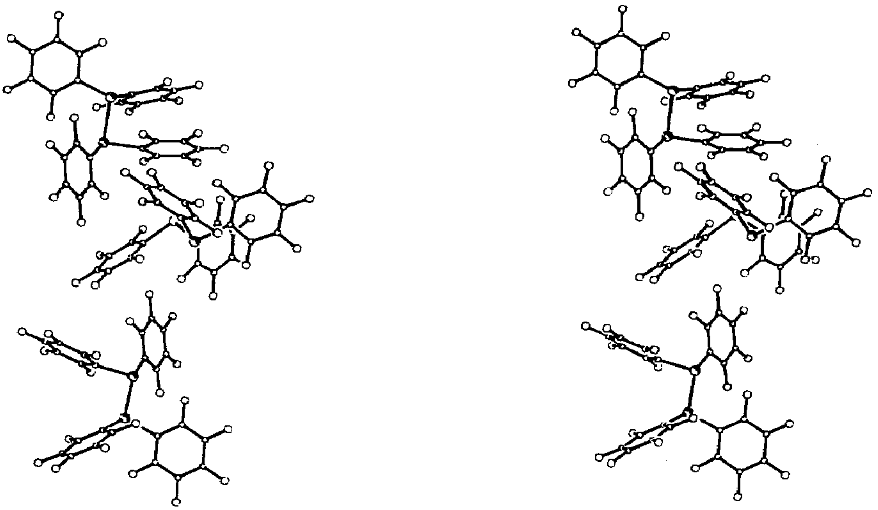

Fig. 2. Stereoview of the arrangement of the three crystallographically independent molecules of **1**.

angles are 66.1 and 99.0°, which indicate about a 16.5° rotation from a perfect *trans* conformation if it may be assumed that for a perfect *trans* conformation these angles would be equal. In contrast, for the only other crystallographically characterized acyclic diarsine, $[(CH_3)_3Si]_4As_2$ [7], the comparable angles are 22.0 and 130.6°, resulting in a much greater, 54.3°, rotation from a *trans* conformation and approaching a *gauche* conformation. Additionally, $(CF_3)_4As_2$ is found by both PES and vibrational spectroscopy to be exclusively *trans* [5], and $(CH_3)_4As_2$ is predominantly (88%) *trans* [8]. The structures of two cyclic diarsines show that a tetramethylbiarsoyl [3a] has a *gauche* conformation, and a diarsahexaphosphabicyclobutane [3b] has a *trans* conformation.

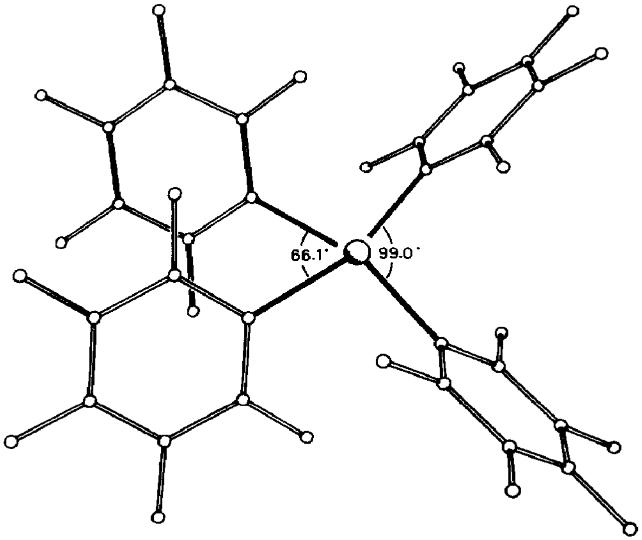

Fig. 3. A view of **1** along the As–As(a) bond with the average C–As–As′–C′ torsion angles.

Table 8

Pentafluorophenyl ring plane orientations to arsenic basal plane

	Basal plane	Phenyl ring	Twist angle (deg)
1 (mol. A)	As(1′), C(16), C(26)	C(11)–C(16)	33.6
		C(21)–C(26)	83.4
1 (mol. B)	As(2′), C(36), C(46)	C(31)–C(36)	75.5
		C(41)–C(46)	33.3
1 (mol. C)	As(3′), C(56), C(66)	C(51)–C(56)	92.6
		C(61)–C(66)	30.7
2	O, C(6), C(12)	C(1)–C(6)	32.8
		C(7)–C(12)	95.1
3	C(6), C(16), C(26)	C(1)–C(6)	41.3
		C(11)–C(16)	41.7
		C(21)–C(26)	70.9

Contrary to expectation, the ^{19}F NMR spectrum for **1** in $CHCl_3$ has been interpreted as evidence for two rotamers, presumed to be *trans* and *gauche* [2]. However, given the general trends for dipnictines, and the specific evidence for diarsines, the contradictory prediction of an exclusive *trans* (or near to *trans*) conformation for **1** in solution (as we have determined for the solid state) could be made with some confidence. Cowley and Dewar have also found the solution data puzzling [5]. We offer this explanation: the minor set of signals seen in solution and attributed to the *gauche* isomer are due instead to the diarsenic oxide, **2**, whose ^{19}F NMR spectrum may be superimposed on that reported for one of the sets of diarsine resonances.

The prediction that the conformation should approach the *trans* limit is further indicated by the very long As–As bond found in **1**. At (av) 2.479(4) Å, it is the longest As–As bond known for any organoarsenic compound. In $[(CH_3)_3Si]_4As_2$ the As–As distance is 2.458(1) Å [7]. Despite the unusual phenyl ring twists evident in Fig. 1 and 2 and Table 8, and the long As–As distance, there are no unusually short F ··· F contacts to suggest that crowding is occurring in these molecules. From the values listed in Table 8, the ring twist angles for **1** are similar to those in **2** which has, by the presence of the oxide bridge, greater steric freedom.

Tetrakis(pentafluorophenyl)arsenic(III) oxide

$(C_6F_5)_2AsOAs(C_6F_5)_2$ (**2**) crystallizes in the monoclinic space group $C2/c$ with one half-molecule comprising the asymmetric unit (Fig. 4, 5); as in **1**, a two-fold axis, in this case containing the O atom and bisecting the As–O–As′ angle, relates the two halves.

The As–O–As′ angle in **2**, 116.2(3)°, is considerably smaller than the 137(2)° angle found in bis(diphenyl)arsenic(III) oxide [9]. The unusually large angle in $(Ph_2As)_2O$ was attributed to $(p \rightarrow d)\pi$ interactions. Bis(diphenyl)antimony(III) oxide, which crystallizes in a lattice isomorphous to its As congener, has a much smaller Sb–O–Sb angle of 122° [10]. Thus, while a variety of arguments could be put forward "explaining" these angles, it would appear that the very adaptable nature of oxide linkages allows a domination of packing forces in angle determination. Furthermore, if $(p \rightarrow d)\pi$ arguments were operative, the greater electronegativity of C_6F_5 vs. C_6H_5 should enhance the effect and lead to a larger As–O–As angle.

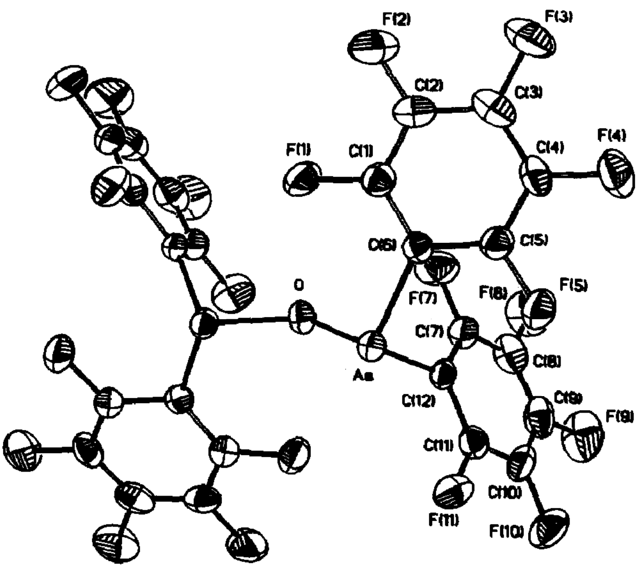

Fig. 4. Molecular structure and numbering scheme for $(C_6F_5)_2AsOAs(C_6F_5)_2$ (**2**). A crystallographic two-fold axis contains the oxygen atom and is in the As–O–As(a) plane.

The As–O–As angle in **2** is also smaller than that found in As_4O_6 (128°) [11] and in *o*-phenylenediarsine oxychloride (121.3(3)°) [12]. Both the As–C and As–O bond distances in **2** are much longer than in $[(C_6H_5)_2As]_2O$; in **2** the As–C distance is (av) 1.968(6) Å, while in $[(C_6H_5)_2As]_2O$, the distance is (av) 1.90 Å, and the As–O distance in **2** is 1.792(3) Å, compared to (av) 1.67 Å. However, the As–C distance in **2** is typical of the other structures in this paper and the unfluorinated triarylarsines quoted in the next section. Such results suggest that minor, but significant, systematic errors exist in the data for the structure of $[(C_6H_5)_2As]_2O$ which was only refined to R = 18% and did not include a correction for absorption or anisotropic refinement.

Comparisons of the phenyl ring twist angles between **1** and **2** (Table 8) show a related pattern. In each of the $(C_6F_5)_2As$ groups of both structures, one ring makes a shallow, 31–34°, angle to the basal plane, while the other is much more nearly perpendicular to it. The absence of a major difference between the twist angles for **1** and **2** suggests that the effect is largely due to steric effects within each $(C_6F_5)_2As$ group and not with the third As substituent.

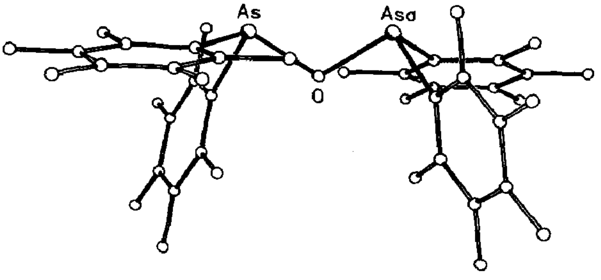

Fig. 5. A view of **2** emphasizing the unusual orientation of the plane of the C(1)–C(6) phenyl ring.

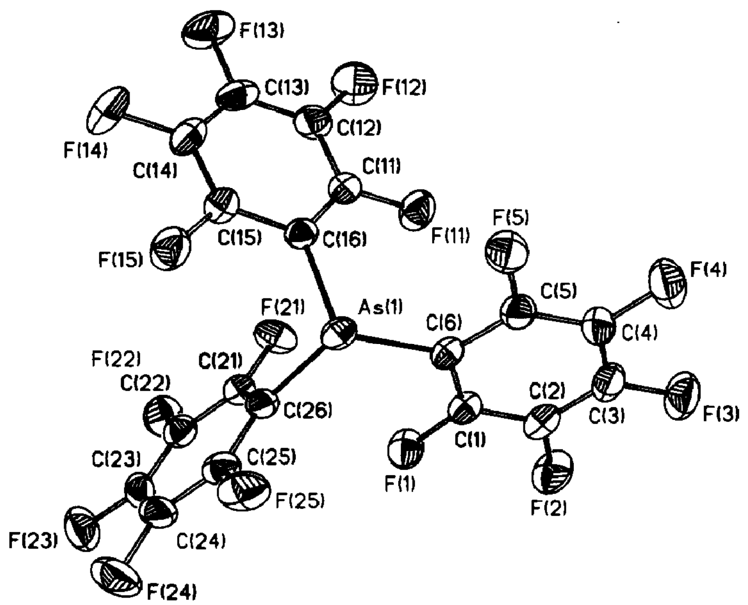

Fig. 6. The molecular structure and labeling scheme for $(C_6F_5)_3As$ (3).

Tris(pentafluorophenyl)arsine

$(C_6F_5)_3As$ (3) crystallizes with a single molecule forming the asymmetric unit (Fig. 6). When compared to other triarylarsines, 3 is found to possess molecular parameters that are unremarkable. The (av) C–As distance, 1.959(3) Å, is typical of most triphenylarsines: *p*-Cl, 1.954(5) Å; *p*-OMe, 1.963(4) Å; and *p*-Me, 1.954(4) Å [13], although all are significantly shorter than that found in the sterically dominated structure of $(mesityl)_3As$, 1.976(5) Å [14]. The C–As–C angles in 3, 96.6(2), 101.1(2) and 101.7(2)° differ from each other by more than any of the other triarylarsines, although the average value, 100.5°, is very similar to those found in other triarylarsines: *p*-Cl, (av) 99.8; *p*-OMe, 98.3; *p*-Me, 99.3° [13]. In $(mesityl)_3As$, the C–As–C angle opens to (av) 107.6(3)° [14].

Of particular interest is the angle of rotation of the plane of the phenyl rings to the plane formed by the three ipso carbon atoms (Table 8). For 3, these angles are C(1–6), 41.3°; C(11–16), 41.7°; and C(21–26), 70.9° with an average of 51.3°. Both of the *p*-Me and *p*-OMe derivatives have three-fold symmetry and single twist angles of 53.4° and 52.4°, respectively [13]. For the *p*-Cl derivative, the range of twist angles exceeds that found in 3: 22.1, 59.9 and 83.6° although the average, 55.2°, is similar. For the sterically crowded $(mesityl)_3As$, which crystallizes with two independent molecules, the range for one molecule is 39.5 to 54.4°, the other 45.6 to 47.3°, with averages of 46.8 and 46.2°, respectively [14]. Except to note that mesityl groups are involved in smaller average twist angles (more deviation from perpendicularity) due to crowding of the ortho methyl groups, little reason can be found for the enormous variation in the observed twist angles. Neither the range nor the average values for 3 would appear unusual in this context.

Acknowledgement

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