Preparation and Crystal Structures of $[As(CF_3)_2O(OH)]_2$, $[As(CF_3)O(OH)Cl]_2$, and $As_4(CF_3)_6O_6(OH)_2$; † a Novel Cage Structure containing Four- and Six-co-ordinated Arsenic

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The compounds $[As(CF_3)_2O(OH)]_2$ (1) and $As_4(CF_3)_6O_6(OH)_2$ (3) have been prepared by oxidative hydrolysis of $As(CF_3)_3$, and a mixture of $As(CF_3)I_2$ and $As(CF_3)_2I$, respectively; $[As(CF_3)O(OH)Cl]_2$ (2) was isolated from the reaction of compound (3) with $SiMe_3Cl$. Crystals of compound (1) are triclinic, space group $P\bar{1}$, a = 584.2(1), b = 703.7(1), c = 958.6(1) pm, α = 103.91(1), β = 103.10(1), γ = 107.90(1)°, and Z = 1. Crystals of compounds (2) and (3) are monoclinic, space group $P2_1/n$, with a = 554.3(1), b = 934.5(2), c = 1 149.6(2) pm, β = 92.70(1)°, and Z = 2 for (2), and a = 880.3(2), b = 1 011.4(2), c = 1 256.7(3) pm, β = 104.17(2)°, and Z = 2 for (3). The structures were refined to R = 0.036, 0.038, and 0.046 for 1 520, 749, and 1 328 unique observed diffractometer data for compounds (1), (2), and (3), respectively. All three molecules have centrosymmetric structures with four-membered $(AsO)_2$ rings. In compounds (1) and (2) the rings bridge equatorial and axial positions of the trigonal-bipyramidal co-ordinated arsenic atoms; the equatorial ring As–O bonds are much shorter than the axial ring As–O bonds. The structures may be interpreted as intermediate stages in a dimerisation reaction pathway. Compound (3) possesses a novel cage structure involving octahedrally and tetrahedrally co-ordinated arsenic, and an $(AsO)_4$ ring in which the As^{III}–O bonds are much shorter than As^{V}–O bonds.

Thermal condensation [1–3] of $M(AsF_5)OH$ (M = Na or K) yields the compounds $[M(AsF_4)O]_2$, which were shown by *X*-ray structure determinations [4–6] to contain four-membered $(AsO)_2$ rings with six-co-ordination of arsenic. It appears that when electron-withdrawing groups are attached to arsenic, the co-ordination number six is generally favoured. This has prompted us to examine As–O heterocycles in which trifluoromethyl substituents are the electron-withdrawing groups. We report here the preparation of $[As(CF_3)_2O(OH)]_2$ (1) and $[As(CF_3)O(OH)Cl]_2$ (2), which contain four-membered $(AsO)_2$ rings, and a novel cage molecule $As_4(CF_3)_6O_6(OH)_2$ (3), together with their structural elucidation by single-crystal *X*-ray diffraction.

Experimental

Materials.—The iodoarsines $As(CF_3)I_2$ and $As(CF_3)_2I$ were prepared by literature methods.[7,8] Chlorotrimethylsilane and unstabilised hydrogen peroxide (35%) were commercial products (Merck AG) which were used without further purification.

Apparatus.—Infrared spectra were obtained with a Perkin-Elmer model 180 spectrometer and are accurate to ±1 cm^{-1}. Bruker WP80SY and 60E spectrometers were used to obtain ^{19}F n.m.r. spectra [$CFCl_3$ internal standard for (1) and (2), external for (3)]. Field ionisation and electronic ionisation mass spectra were obtained on a Varian CH5 instrument.

Preparation of $[As(CF_3)_2O(OH)]_2$ (1).—Water (10 cm^3) and unstabilised hydrogen peroxide (35%, 10 cm^3) were added to $As(CF_3)_3$ (10 g) at 5 °C, and the mixture was stirred for 1 h at room temperature. No exothermic reaction was observed, and two liquid layers were present. When more water (20 cm^3) was added and the mixture allowed to stand for 12 h, the lower layer [unchanged $As(CF_3)_3$] disappeared almost completely. Compound (1) separated out as colourless crystals and was characterised by *X*-ray structure determination (yield 0.5 g, m.p. 135 °C); ^{19}F n.m.r. (in CH_2Cl_2), $\delta(CF_3)$ −63.2 p.p.m. I.r. (Nujol mull): 3 500—3 300(br) vw, 2 952vs, 2 920vs, 1 660vw, 1 450m, 1 376w, 1 182m, 1 148m, 1 134m, 1 108m, 1 024vw, 910vw, 872vw, 782w, and 740w cm^{-1}. Mass spectrum: $(M - CF_3)^+$, m/z = 423.

Preparation of $[As(CF_3)O(OH)Cl]_2$ (2).—Chlorotrimethylsilane (0.34 g) was added to a suspension of $As_4(CF_3)_6O_6(OH)_2$ (3) (0.3 g) in anhydrous CH_2Cl_2 (10 cm^3), and the mixture was stirred for 12 h. The mixture was filtered, and the volume of the clear solution was reduced to half *in vacuo*. On keeping this solution at −30 °C for 24 h, crystals of the chloro-compound (2) formed (yield 0.1 g; m.p. 140 °C, sealed capillary). Compound (2) was characterised by *X*-ray analysis; ^{19}F n.m.r. (CH_2Cl_2), $\delta(CF_3)$ −64.0 p.p.m. I.r. (Nujol): 2 960vs, 2 930s, 2 860vs, 1 452m, 1 378w, 1 200vw, 1 170 (sh), 1 158w, 1 135w, 775w, 742w, and 722w cm^{-1}.

Preparation of $As_4(CF_3)_6O_6(OH)_2$ (3).—A mixture of the iodoarsines $As(CF_3)I_2$ (3.2 g, 8.0 mmol) and $As(CF_3)_2I$ (2.8 g, 8.2 mmol), previously cooled to −10 °C, was treated with unstabilised hydrogen peroxide (35%, 5 cm^3) and water (5 cm^3). An exothermic reaction occurred at room temperature and the mixture was cooled intermittently with ice. After 30 min, water (20 cm^3) was added, and the iodine formed was filtered off. The solution was evaporated *in vacuo* over sulphuric acid (8 d). Transparent crystals, corresponding to a hydrate of approximate composition $As_4(CF_3)_6(OH)_{14}$ (M^+, m/z = 952), first separated out and on further evaporation changed to a white powder (2.5 g). The white powder was dissolved in hot chloroform (150 cm^3) and maintained at 5—10 °C to allow the chloroform to evaporate slowly. Compound (3) (1.3 g) separated out as a crude product after 3 d. On recrystallisation from hot chloroform, colourless crystals of $As_4(CF_3)_6O_6(OH)_2$ (3) were obtained, which were used for the *X*-ray analysis (yield 0.8 g, m.p. 215 °C) (Found:

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† Di-μ-oxo-bis[hydroxobis(trifluoromethyl)arsenic], di-μ-oxo-bis-[chloro(hydroxo)trifluoromethylarsenic] and di-μ-oxo-di-μ-(trifluoromethylarsonato-*OO'*)-bis[bis(trifluoromethyl)arsenic].

Supplementary data available (No. SUP 23974, 31 pp.): thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Crystal data and structure refinement details

Compound	(1)	(2)	(3)
Formula	$[As(CF_3)_2O(OH)]_2$	$[As(CF_3)O(OH)Cl]_2$	$As_4(CF_3)_6O_6(OH)_2$
M	491.88	424.77	843.73
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a/pm	584.2(1)	554.3(1)	880.3(2)
b/pm	703.7(1)	934.5(2)	1 011.4(2)
c/pm	958.6(1)	1 149.6(2)	1 256.7(3)
α/°	103.91(1)		
β/°	103.10(1)	92.70(1)	104.17(2)
γ/°	107.90(1)		
U/nm^3	0.3442	0.5948	1.0848
Z	1	2	2
D_c/Mg m^{-3}	2.373	2.371	2.583
$F(000)$	232	400	792
Number of reflections			
Measured	1 675	1 341	1 645
Unique	1 675	776	1 420
Observed [$F > 3\sigma(F)$]	1 520	749	1 328
Crystal size/mm	0.2 × 0.2 × 0.3	0.3 × 0.2 × 0.1	0.2 × 0.3 × 0.6
μ(Mo-K_α)/mm^{-1}	4.99	6.13	6.28
R	0.036	0.038	0.046
R' [a]	0.041	0.046	0.049
g [b]	0.000 58	0.001 93	0.000 78
Maximum residual electron density/e pm^{-3} × 10^{-7}	5.8	6.4	9.1

[a] $\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|$. [b] For $w^{-1} = \sigma^2(F) + gF_o^2$.

Table 2. Atomic co-ordinates (× 10^4) for $[As(CF_3)_2O(OH)]_2$ (1) with estimated standard deviations in parentheses

Atom	x	y	z
As	1 562(1)	844(1)	1 557(1)
O(1)	1 327(5)	−731(4)	−544(3)
O(2)	4 763(8)	2 919(7)	1 812(5)
C(1)	1 137(9)	2 220(7)	3 554(5)
C(2)	1 763(10)	−1 730(7)	2 022(5)
F(11)	954(6)	4 078(4)	3 566(3)
F(12)	−940(6)	1 069(5)	3 766(3)
F(13)	3 088(6)	2 658(5)	4 777(3)
F(21)	2 415(11)	−1 434(6)	3 481(3)
F(22)	3 471(7)	−2 317(6)	1 526(4)
F(23)	−422(8)	−3 333(5)	1 330(5)

C, 8.4; H, 0.7. $C_6H_2As_4F_{18}O_8$ requires C, 8.5; H, 0.2%); mass spectrum, m/z = 844 (M^+) and 775 ($M - CF_3$)$^+$. ^{19}F N.m.r. (H_2O): $\delta(CF_3)$ −64.7 and −66.5 p.p.m. I.r. (Nujol): 2 968vs, 2 930vs, 2 862vs, 1 460s, 1 376m, 1 135s, br, 912w, 882w, 828m, 819s, 758vw, 740vw, and 728w cm^{-1}.

Crystal Structure Determinations.—The crystal data and details of the *X*-ray analysis for compounds (1)—(3) are presented in Table 1. Data were collected to 2θ = 45° by a profile-fitting procedure[9] on a Stoe–Siemens four-circle diffractometer using graphite-monochromated Mo-K_α radiation (λ = 71.069 pm).

The structures were solved by direct [compounds (1) and (3)] and Patterson [compound (2)] methods, and refined anisotropically with complex neutral-atom scattering factors. The hydroxy-hydrogen atoms were not located. Two of the CF_3 groups in (3) were disordered; the occupation factors p refined to 0.665(10) for F(4), F(5), and F(6) [$1 - p$ for F(10), F(11), and F(12)], and 0.590(8) for F(7), F(8), and F(9) [$1 - p$ for F(13), F(14), and F(15)]. Weighting schemes and final R values are given in Table 1. A Data General Eclipse minicomputer was used for all calculations, using programs written by G. M. S. Final atomic co-ordinates are given in Tables 2—4, and derived molecular dimensions in Tables 5—7.

Table 3. Atomic co-ordinates (× 10^4) for $[As(CF_3)O(OH)Cl]_2$ (2) with estimated standard deviations in parentheses

Atom	x	y	z
As	622(1)	6 380(1)	5 375(1)
Cl	−1 531(3)	8 296(2)	5 872(2)
O(1)	2 651(12)	7 364(6)	4 314(6)
O(2)	1 976(6)	4 520(4)	5 048(3)
C	1 991(12)	6 119(6)	7 010(5)
F(1)	4 157(7)	5 536(4)	7 003(3)
F(2)	574(8)	5 289(5)	7 578(3)
F(3)	2 218(9)	7 337(4)	7 587(4)

Results and Discussion

Attempts to prepare bis(trifluoromethyl)arsinous acid by stepwise hydrolysis of tris(trifluoromethyl)arsine were unsuccessful.[10] This arsine is stable to water, but undergoes slow oxidative hydrolysis with aqueous hydrogen peroxide [reaction (i)].

$$2As(CF_3)_3 \xrightarrow[-H_2O,\ 12\ h]{H_2O_2} \underset{(1)}{[As(CF_3)_2O(OH)]_2} + 2CHF_3 \quad \text{(i)}$$

An equimolar mixture of the iodoarsines $As(CF_3)I_2$ and $As(CF_3)_2I$ undergoes exothermic oxidative hydrolysis when similarly treated with aqueous hydrogen peroxide [reaction (ii)]. Formation of compound (3) appears to take place through

$$2As(CF_3)I_2 + 2As(CF_3)_2I \xrightarrow[-H_2O]{H_2O_2} \underset{(3)}{As_4(CF_3)_6O_6(OH)_2} + 3I_2 \quad \text{(ii)}$$

Table 4. Atomic co-ordinates (× 10^4) for $As_4(CF_3)_6O_6(OH)_2$ for (3) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
As(1)	6 088(1)	−546(1)	−508(1)
As(2)	6 962(1)	2 055(1)	696(1)
C(1)	8 061(8)	−1 615(8)	120(7)
C(2)	7 256(7)	3 828(7)	134(6)
C(3)	6 253(9)	−549(8)	−2 087(7)
O(1)	7 277(4)	1 043(4)	−301(4)
O(2)	4 216(5)	340(4)	−873(3)
O(3)	4 930(5)	−2 155(4)	−749(4)
O(4)	8 437(9)	1 834(9)	2 082(6)
F(1)	6 956(7)	4 727(5)	798(5)
F(2)	8 681(5)	3 986(5)	6(5)
F(3)	6 267(6)	4 033(6)	−829(4)
F(4)	9 076(10)	−1 427(13)	−459(9)
F(5)	7 887(13)	−2 831(11)	205(20)
F(6)	8 811(13)	−1 122(13)	1 102(8)
F(7)	6 779(14)	−1 762(10)	−2 332(8)
F(8)	7 125(25)	330(14)	−2 342(11)
F(9)	4 857(10)	−519(12)	−2 739(6)
F(10)	8 130(33)	−2 604(31)	−696(17)
F(11)	7 800(26)	−2 425(23)	868(16)
F(12)	9 322(24)	−1 108(23)	253(44)
F(13)	5 690(17)	609(17)	−2 618(10)
F(14)	7 770(19)	−449(24)	−2 122(16)
F(15)	5 735(22)	−1 468(17)	−2 679(12)

Table 5. Bond lengths (pm) and angles (°) for $[As(CF_3)_2O(OH)]_2$ (1) *

As–O(1)	200.3(10)	As–O(2)	190.6(10)
As–C(1)	203.4(11)	As–C(2)	199.8(11)
As–As′	285.4(14)	As–O(1′)	171.3(9)
C(1)–F(12)	132.5(9)	C(1)–F(11)	134.2(9)
C(2)–F(21)	130.9(9)	C(1)–F(13)	133.1(8)
C(2)–F(23)	130.9(8)	C(2)–F(22)	132.9(10)

O(1)–As–O(2)	90.5(3)	O(1)–As–C(1)	170.2(3)
O(2)–As–C(1)	98.2(3)	O(1)–As–C(2)	84.7(3)
O(2)–As–C(2)	114.4(4)	C(1)–As–C(2)	95.6(4)
O(1)–As–O(1′)	80.0(3)	O(2)–As–O(1′)	124.6(3)
C(1)–As–O(1′)	91.3(3)	C(2)–As–O(1′)	118.7(3)
As–O(1)–As′	100.0(3)	As–C(1)–F(11)	109.0(4)
As–C(1)–F(12)	113.4(4)	F(11)–C(1)–F(12)	107.0(5)
As–C(1)–F(13)	114.0(5)	F(11)–C(1)–F(13)	106.2(4)
F(12)–C(1)–F(13)	106.9(5)	As–C(2)–F(21)	112.6(4)
As–C(2)–F(22)	111.5(5)	F(21)–C(2)–F(22)	106.7(6)
As–C(2)–F(23)	110.3(5)	F(21)–C(2)–F(23)	109.1(6)
F(22)–C(2)–F(23)	106.4(5)		

* Here and in Tables 6 and 7 a prime (′) indicates symmetry-equivalent atoms generated by the action of an inversion centre at the centre of the molecule.

Table 6. Bond lengths (pm) and angles (°) for $[As(CF_3)O(OH)Cl]_2$ (2)

As–Cl	224.0(2)	As–O(1)	193.1(7)
As–O(2)	193.7(3)	As–C	200.8(6)
As–As′	279.5(2)	C–F(1)	131.0(7)
O(2)–As′	171.8(3)	C–F(3)	132.0(7)
C–F(2)	130.1(8)		

Cl–As–O(1)	96.5(2)	Cl–As–O(2)	169.3(1)
O(1)–As–O(2)	93.6(2)	Cl–As–C	92.3(2)
O(1)–As–C	116.3(3)	O(2)–As–C	86.6(2)
Cl–As–O(2′)	90.8(1)	O(1)–As–O(2′)	124.0(2)
O(2)–As–O(2′)	80.4(2)	C–As–O(2′)	118.7(2)
As–O(2)–As′	99.6(2)	As–C–F(1)	110.4(2)
As–C–F(2)	109.4(4)	F(1)–C–F(2)	109.1(5)
As–C–F(3)	112.9(4)	F(1)–C–F(3)	107.1(5)
F(2)–C–F(3)	107.9(5)		

progressive dehydration *in vacuo* of a compound of composition $As_4(CF_3)_6(OH)_{14}$, which is initially formed. Attempts to crystallise the intermediate products were unsuccessful. Compound (3) is only slightly soluble in water, chloroform, and dichloromethane, but could be recrystallised from hot chloroform. It decomposes in hot water to yield a mixture of trifluoromethylarsonic and bis(trifluoromethyl)arsinic acids; two ^{19}F n.m.r. signals in the intensity ratio 1 : 2 were observed.

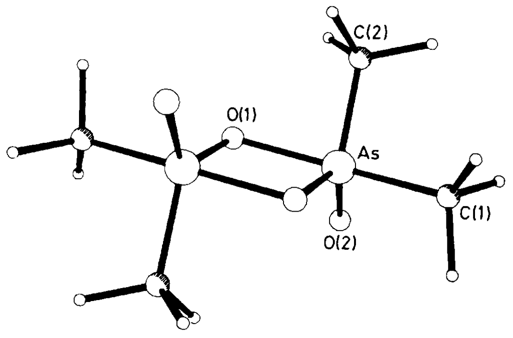

Figure 1. The molecule of $[As(CF_3)_2O(OH)]_2$ (1), with the unique atoms (except F) labelled

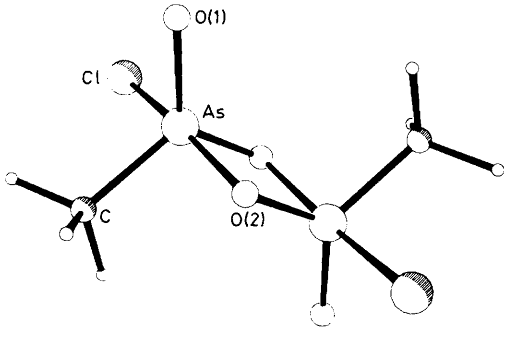

Figure 2. The molecule of $[As(CF_3)O(OH)Cl]_2$ (2), with the unique atoms (except F) labelled

The field ionisation and electronic ionisation mass spectra of compound (3) exhibit a prominent $(M - CF_3)^+$ peak at *m*/*z* 775, and a weak molecular ion at *m*/*z* 844. The compound $[As(CF_3)O(OH)Cl]_2$ (2) was isolated from the reaction of compound (3) with $SiMe_3Cl$; it did not prove possible to characterise the other products of this unusual reaction.

The molecular structures of compounds (1)—(3) are shown in Figures 1—3. All three molecules lie on crystallographic inversion centres, and so in each case the asymmetric unit consists of half a molecule. The structures of compounds (1) and (2) are very similar; the arsenic atom is trigonal-bipyramidally co-ordinated, with equatorial trifluoromethyl and hydroxy-groups. The four-membered ring bridges equatorial and axial positions, and the remaining axial position is occupied by a trifluoromethyl group in (1) and a chlorine atom in (2). The four-membered rings each involve long [200.3 and 193.7 pm in (1) and (2) respectively] axial As–O bonds

Table 7. Bond lengths (pm) and angles (°) for $As_4(CF_3)_6O_6(OH)_2$ (3), omitting the two disordered CF_3 groups

As(1)–C(1)	203.4(7)	As(2)–O(1)	169.3(5)	As(1)–O(2)	183.3(4)	As(2)–O(4)	191.4(7)
As(1)–O(1)	190.1(4)	As(2)–O(3′)	168.6(5)	As(1)–As(1′)	277.7(1)	C(2)–F(1)	130.4(10)
As(1)–O(3)	190.5(4)	C(2)–F(2)	131.3(9)	As(2)–C(2)	196.7(7)	C(2)–F(3)	132.3(8)
As(1)–O(2′)	183.1(5)	As(1)–C(3)	202.4(9)				

C(1)–As(1)–C(3)	96.9(3)	As(1)–O(1)–As(2)	115.4(3)	O(1)–As(1)–O(2′)	88.7(2)
C(3)–As(1)–O(1)	88.1(3)	As(1)–O(3)–As(2′)	116.0(3)	O(3)–As(1)–O(2′)	92.9(2)
C(3)–As(1)–O(2)	91.8(3)	As(2)–C(2)–F(2)	111.6(5)	C(2)–As(2)–O(4)	108.3(3)
C(1)–As(1)–O(3)	88.9(3)	As(2)–C(2)–F(3)	110.9(5)	C(2)–As(2)–O(3′)	100.2(3)
O(1)–As(1)–O(3)	178.2(2)	F(2)–C(2)–F(3)	107.7(6)	O(4)–As(2)–O(3′)	115.3(3)
C(3)–As(1)–O(2′)	172.3(3)	C(1)–As(1)–O(1)	90.4(2)	As(1)–O(2)–As(1′)	98.6(2)
O(2)–As(1)–O(2′)	81.4(2)	C(1)–As(1)–O(2)	170.8(3)	As(2)–C(2)–F(1)	109.9(5)
C(2)–As(2)–O(1)	103.0(3)	O(1)–As(1)–O(2)	93.0(2)	F(1)–C(2)–F(2)	110.0(6)
O(1)–As(2)–O(4)	114.0(3)	C(3)–As(1)–O(3)	90.4(3)	F(1)–C(2)–F(3)	106.5(6)
O(1)–As(2)–O(3′)	114.1(2)	O(2)–As(1)–O(3)	88.0(2)		

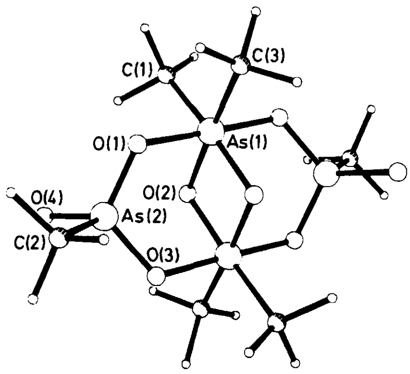

Figure 3. The molecule of $As_4(CF_3)_6O_6(OH)_2$ (3), with the unique atoms (except F) labelled

and short equatorial (171.3 and 171.8 pm) As–O bonds. However, the axial As–C bond in (1) (203.4 pm) is only slightly longer than the equatorial As–C bonds [199.8 and 200.8 pm in compounds (1) and (2) respectively].

In both molecules the equatorial As–C and As–OH bonds are bent out of the equatorial plane, towards the long axial As–O bond. This is consistent with a contribution from an extreme resonance structure in which the short ring As–O bond is replaced by As=O, and the long ring As–O bond deleted. This 'adduct' of two monomers would require tetrahedral geometry at arsenic, and explains the observed unequal bonds in the $(AsO)_2$ ring and the distortions from idealised trigonal-bipyramidal geometry.

The molecule of compound (3) approximates closely to $2/m$ (C_{2h}) symmetry with the two-fold axis passing through the two octahedrally co-ordinated arsenic atoms. The bond lengths in the four-membered $(AsO)_2$ ring are equal (183.1 and 183.3 pm) whereas the As(1)–O–As(2) bridges are very unsymmetrical, the four-co-ordinated As(2) having much shorter bonds (169.3 and 168.6) than the six-co-ordinated As(1) (190.1 and 190.5 pm). This will tend to equalise the effective oxidation states, which are nominally +3 (with a net charge of +1) and +5 (net charge −1) respectively. The trifluoromethyl groups are also more tightly bonded to the four-co-ordinated arsenic (196.7) than the six (202.4 and 203.4 pm). The As–OH bonds are similar and long in all three compounds, confirming the assignment of the hydrogen atoms. The polymeric structure of AsO_2 also contains arsenic atoms in the +3 and +5 oxidation states linked by oxygen, but the co-ordination numbers are lower (three and four respectively),[11] and the cross-linking and terminal As=O bonds (161.1 pm) make it unnecessary to assign formal charges to the atoms. The molecular skeleton of compound (3) is somewhat reminiscent of the $[B_4O_5(OH)_4]^{2-}$ anion found in borax.[12]

The structures reported here indicate that when electron-withdrawing groups are attached to an arsenic atom which is also bonded to oxygen, oligomers containing four-membered $(AsO)_2$ rings are formed in preference to monomers having As=O double bonds, although compounds (1) and (2) may also be considered to be intermediate stages in a monomer–dimer reaction pathway.

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References

1 L. Kolditz and B. Nussbücher, *Z. Anorg. Allg. Chem.*, 1961, **312**, 299.
2 L. Kolditz and D. Renno, *Z. Anorg. Allg. Chem.*, 1962, **315**, 46.
3 L. Kolditz and E. Rosel, *Z. Anorg. Allg. Chem.*, 1965, **341**, 93.
4 H. Dunken and W. Haase, *Z. Chem.*, 1963, **3**, 433.
5 H. Dunken and W. Haase, *Z. Chem.*, 1964, **4**, 156.
6 H. Dunken and W. Haase, Proceedings, 8th International Conference on Chemical Crystallography, Wien, Springer, Wien, 1964, p. 163.
7 G. R. A. Brandt, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1952, 2552.
8 E. G. Walaschewski, *Chem. Ber.*, 1953, **86**, 273.
9 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.
10 H. J. Emeléus, R. N. Haszeldine, and E. G. Walaschewski, *J. Chem. Soc.*, 1953, 1552.
11 P. G. Jones, W. Beesk, G. M. Sheldrick, and E. Schwarzmann, *Acta Crystallogr., Sect. B*, 1980, **36**, 439.
12 A. F. Wells, 'Structural Inorganic Chemistry,' 4th edn., Clarendon Press, Oxford, 1975.

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