Chemistry of Polyfunctional Molecules. Part 86.[1] Organoarsenic Compounds derived from 1,3-Bis(di-iodoarsino)propane with Monocyclic, Tricyclic, and Straight-chain Structures; *X*-Ray Crystal Structure of 2,8,13,14-Tetraoxa-1,3,7,9-tetra-arsatricyclo[7.3.1.1^{3,7}]tetradecane†

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Treatment of $(C_6H_5)_2As(CH_2)_3As(C_6H_5)_2$ (**1**) with HI gives under elimination of benzene $I_2As(CH_2)_3AsI_2$ (**2**). The reduction of (**2**) with sodium in tetrahydrofuran leads to the heterocyclic compound $I\overline{As(CH_2)_3As}I$ (**3**). Hydrolysis of (**2**) yields the new tricyclic compound $(CH_2)_3As_4O_4(CH_2)_3$ (**4**). The oxidative solvolysis of (**2**) with H_2O_2 results in the formation of $(HO)_2OAs(CH_2)_3AsO(OH)_2$ (**5**). All the compounds have been characterized by elemental analysis, i.r., Raman, ^1H n.m.r., and mass spectra and by conductivity measurements. The crystal structure of compound (**4**) has been solved by *X*-ray diffraction. Crystals are monoclinic, space group $P2_1/c$, with a = 6.886(2), b = 14.745(5), c = 11.577(4) Å, β = 94.15(3)°, and Z = 4. Data collection yielded 4 183 reflections, of which 2 026 with $I \geqslant 3\sigma(I)$ gave R = 0.038. The molecule consists of a tricyclic ring system. The main skeleton is an eight-membered As_4O_4 ring comparable to the *endo–endo* structure of N_4S_4. The As atoms are linked together by two $(CH_2)_3$ chains forming an open-envelope conformation. The solid state and a solution of (**4**) in CS_2 show appreciable evidence for the existence of intramolecular C–H ··· O–As bonding.

Alkyltris(di-iodoarsines), such as $CH_3C(CH_2AsI_2)_3$[2] and $[NH(CH_2CH_2AsI_2)_3]I$[3] are important precursors in the synthesis of arsenic- and other hetero element-containing nortricyclanes,[4–8] noradamantanes,[6,8–10] adamantanes,[7,11,12] and spherands.[3] This paper presents the synthesis of 1,3-bis(di-iodoarsino)propane and its reactions to give organoarsenic compounds with monocyclic, tricyclic, and straight-chain structures.

Results and Discussion

1,3-Bis(diphenylarsino)propane, (**1**),[13,14] reacts with HI, by analogy with previous work,[2,3,15] to form 1,3-bis(di-iodoarsino)propane, (**2**), equation (1).

$$\underset{(1)}{(C_6H_5)_2As(CH_2)_3As(C_6H_5)_2} + 4HI \xrightarrow{CH_2Cl_2} 4C_6H_6 + \underset{(2)}{I_2As(CH_2)_3AsI_2} \quad (1)$$

Reduction of (**2**) with sodium in tetrahydrofuran (thf) affords the heterocyclic compound (**3**), which is isolated, after recrystallization from carbon disulphide–dichloromethane, as deep red, air-sensitive microcrystals [equation (2)]. Surprisingly, there is no further reduction of (**2**) or (**3**) to polyarsanes $[(CH_2)_3As_2]_n$, even on the application of an excess of sodium. The mass spectral data [electron impact (e.i.) and field desorption (f.d.)] of compound (**3**) confirm the monomeric structure. The heterocycle (**3**) is therefore a structural analogue of the compound $(C_6H_5)\overline{As(CH_2)_3As}(C_6H_5)$.[16] However, (**3**) exists in two modifications, a red and a brown form. The dimorphism of (**3**) is proven by a differential thermal analysis.

$$\underset{(2)}{I_2As(CH_2)_3AsI_2} + 2Na \longrightarrow 2NaI + \underset{(3)}{I\overline{As(CH_2)_3As}I} \quad (2)$$

When the tetra-iododiarsine (**2**) is allowed to react with $H_2O–NH_3$ in thf [equation (3)], the tricyclic compound (**4**) is formed. On recrystallization from methanol–diethyl ether or water, colourless crystals of (**4**) are obtained.

$$\underset{(2)}{2I_2As(CH_2)_3AsI_2} + 8NH_3 + 4H_2O \longrightarrow 8NH_4I + \underset{(4)}{(CH_2)_3As_4O_4(CH_2)_3} \quad (3)$$

The solubility of (**4**) in water increases after the addition of KOH, presumably due to cleavage of the As_4O_4 ring and formation of $-CH_2As(OH)O^-$ groups. This assumption is confirmed by the ^1H n.m.r. spectrum, since only one multiplet for the methylene groups is observed. Finally a viscous substance results, from which no pure compound can be isolated.

Oxidative hydrolysis of (**2**) with dilute hydrogen peroxide yields $(HO)_2OAs(CH_2)_3AsO(OH)_2$ (**5**). The first pK_a value of (**5**) is 4.1, whereas the second value of 8.8 is regarded only as an approximation, due to buffering effects.

The formulation of compounds (**1**)—(**5**) follows from elemental analysis, mass, ^1H n.m.r. (see Experimental section), i.r., and Raman spectra (Table 1). Furthermore, the structure of (**4**) has been determined by *X*-ray crystallography (see below). Whereas mass spectra of compounds (**1**), (**3**), and (**4**) exhibit the

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† *Supplementary data available* (No. SUP 56454, 8 pp.): thermal parameters, H-atom co-ordinates, least-squares planes data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Characteristic i.r. and Raman spectroscopic data[a] (cm^{-1}) for $I_2As(CH_2)_3AsI_2$ (**2**), $I\overline{As(CH_2)_3As}I$ (**3**), $(CH_2)_3As_4O_4(CH_2)_3$ (**4**), and $(HO)_2OAs(CH_2)_3AsO(OH)_2$ (**5**)

	(**2**)		(**3**)		(**4**)		(**5**)	
Assignments	I.r.[b]	Raman	I.r.[b,c]	Raman[c]	I.r.[b]	Raman	I.r.[b]	Raman
ν(CH$_2$)		2 960vw			2 960w	2 962w	2 960w	2 960vw
		2 950vw	2 940w		2 945w–m	2 947m	*d*	
		2 918w			2 928w	2 925w–m	*d*	2 934w
		2 904w			2 900w–m	2 900s	*d*	
	2 880w,br	2 886w	2 880w		2 880w–m	2 881s	*d*	
		2 858w	2 830w		2 850w–m	2 856m	*d*	
ν(OH ··· OAs)							2 770s,br	
							2 320s,br	
δ(CH$_2$)	1 438w	1 442w	1 433w		1 450w–m	1 450w	1 451w–m	1 458w
	1 395w	1 402w	1 406w		1 403w–m	1 410w	1 423vw	
	1 390w	1 380w	1 389w		1 395w–m	1 391w–m	1 398m	1 404w
γ(CH$_2$)	1 322w	1 306w	1 315w		1 322w		1 350w	1 318vw
					1 290w	1 281w		
					1 280s			
	1 225w	1 234vw	1 240w		1 235m	1 235m	1 252w	1 263w
δ(OH ··· OAs)							1 227s,br	
							1 215(sh)	
γ(CH$_2$)	1 200w	1 204w–m	1 210w		1 222w–m	1 224w–m	1 190w–m	
	1 143w	1 146w	1 180w		1 215w		1 175w–m	
CH$_2$ ring deformation					1 128m			
					1 120w–m			
					1 100w			
ν(CC)		1 060vw	1 015w		1 070vw	1 082vw	1 092vw	1 026w
	1 018w	1 025vw	925w	925w	1 060vw	1 067vw	1 020vw	1 012w
					1 050vw			
					1 025w	1 028w		
ρ(CH$_2$)		997w	880w		951m	947w–m	965w–m	
					942m			
	910w	916w	800w		883m	880w–m	884w	
ν(As=O)							900vs,br	
								848m,br
ν(As–O)					796(sh)	798w–m		
					780m–s	780vw	780s	
					760s	752w	760(sh)	762w–m
					720vs	716w	710m	722s
ν(AsC)	685w–m	672m	555w		555w–m	556m	621w–m	625w–m
	538w	547w	530w–m	540w	528m–s	532vs		
					512m–s	516m		
					470m	470s		
δ(C–C–C)	365w	347w	435w	434w	430w–m	428m	415m	414(sh)
					383w	386m	395s	399w–m
							365vw	366w
δ(C–As–O)					315w	320(sh)	330m–s	346w
						306w–m	300w	320w
					291w	296w–m	280w	286w–m
						272w		
					255w–m	254w–m	260w	252w–m
ν(AsAs)				250m				
ν(AsI)		229s		214s				
		222s		180m				
		202vs						
		158m						
δ(OAsO)						191vs		202w–m
						178(sh)		168w
						132m		156w
						103s		112w
δ(AsI$_2$)		80s						
		59m–s						

[a] I.r. measured as KBr discs and Raman measured as pure solid products; vs = very strong, s = strong, m = medium, w = weak, vw = very weak, br = broad, sh = shoulder. [b] Recorded between 4 000 and 250 cm^{-1} only. [c] Due to decomposition of the brown modification of (**3**), the red form was measured only. [d] Obscured by ν(OH ··· OAs).

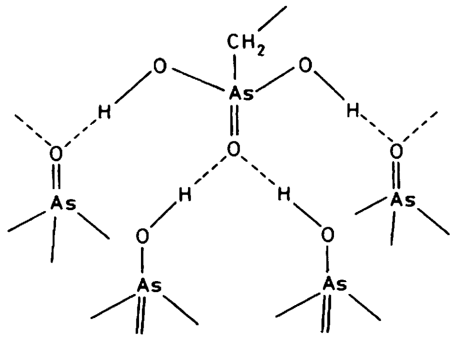

Figure 1. The hydrogen-bonding system proposed for propane-1,3-diarsonic acid (5)

molecular ions (M^+), for compound (2) only the (M^+ − I) ion is recorded as the peak of highest mass. The vibrational spectra of the diarsonic acid (5) give evidence for strong associations by short hydrogen bonds in the solid state; thus evaporation and ionisation of (5), even in the direct inlet system of the mass spectrometer takes place with decomposition. However, from the appearance of the most intense peak due to As_4O_6 beside the (M^+ − H) fragment in the mass spectrum of (5), it is suggested that each $-AsO(OH)_2$ group in the molecule is linked to three or four other $-AsO(OH)_2$ moieties (Figure 1), probably through intermolecular interactions analogous to those observed in $(HO)_2OP(CH_2)_3PO(OH)_2$.[17]

The ^1H n.m.r. spectrum for the monocyclic compound (3) exhibits one multiplet, whereas the tricyclic compound (4) reveals two multiplets at δ 3.1 and δ 1.6 (solvent CS_2) in the intensity ratio of 1:5. The unusual downfield shift of the two CH_2 protons (δ 3.1) can be explained from the structure of (4) (Figure 2) by the interaction of the H(22) and H(52) protons with the O(2) and O(4) oxygen atoms of the As_4O_4 ring. The *X*-ray analysis of (4) confirms such a conclusion as the average distance of the calculated hydrogen atoms H(22) and H(52) to the oxygen atoms O(2) and O(4) is 2.6 Å. This fact is of interest because only a few values for C–H ··· O bonds are known at present.[18] Analogous interactions of methylene protons with oxygen atoms of As_4O_4 rings are also found in the spherand $[N(CH_2CH_2)_3]_8(As_4O_4)_6$.[3] In order to confirm the CH_2 ··· OAs interaction in compound (4) its ^1H n.m.r. spectrum was simulated. The observed and computed ^1H n.m.r. spectra (100 MHz) were in good agreement. When $(CH_2)_3As_4O_4(CH_2)_3$ (4) is dissolved in D_2O all the oxygen atoms of the As_4O_4 ring are able to form AsO ··· D_2O bridges. For this reason the ^1H n.m.r. spectrum of such a solution shows only a single multiplet for all the CH_2 protons at δ 1.95 p.p.m.

In the vibrational spectra of compounds (2) and (3), the bands of the aliphatic skeleton appear only with low intensity, caused by the optical dilution of the heavy AsI_2 or AsI moieties. The assignments of the most intense Raman emissions between 250 and 150 cm^{-1} to the AsI stretching modes are based on earlier works.[2,15] In the Raman spectrum of the heterocycle (3) the As–As stretching mode falls into the ν(AsI) region, the assignments of the three bands to the individual modes are therefore tentative. The As–C modes of the cyclic compounds (3) and (4) are shifted to lower wavenumbers compared to those of (1) (Experimental section), (2), and (5). For this reason they are better characterized as ring modes than as local As–C stretchings. The i.r. spectrum of the diarsonic acid (5) exhibits only two broad and intense ν(OH) absorptions at 2 770 and 2 320 cm^{-1}, indicating that all the AsOH bonds are involved in strong hydrogen bonds. By comparison with the polymethylenediphosphonic acids $(HO)_2OP(CH_2)_nPO(OH)_2$ (n = 1—3), which are well characterized by *X*-ray crystallography,[17,19] and which also exhibit two intense and broad ν(OH) absorptions in the same i.r. range,[17,20] we deduce that (5) contains a similar hydrogen-bonding system. The different positions of the ν(As=O) stretching band in the i.r. and Raman spectra of (5) indicate an inversion centre in the solid state.

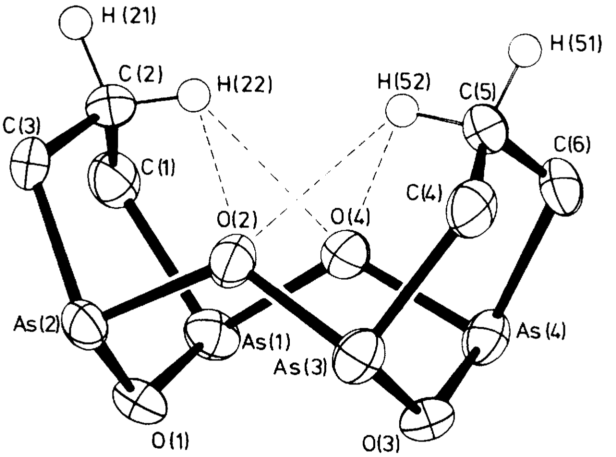

Figure 2. ORTEP view of $(CH_2)_3As_4O_4(CH_2)_3$ (4) with interactions between the CH_2 protons H(22) and H(52) with the oxygen atoms O(2) and O(4)

The crystal-structure determination shows that compound (4) consists of a tricyclic ring system. The main skeleton is an eight-membered As_4O_4 ring comparable to the *endo–endo* structure of N_4S_4.[21] The As atoms are linked together by two $(CH_2)_3$ chains forming an open-envelope conformation (Figure 2). Bond lengths and angles are given in Table 2. The dihedral angle between the least-square planes defined by As(1),As(2), O(2),O(4) and As(3),As(4),O(2),O(4) is 57.3°. The As–O bond lengths range from 1.773(6) to 1.811(6) Å and are slightly shorter than expected for a single bond. The As–C bonds lie in the range 1.939(8)—1.987(9) Å and are close to those reported for similar compounds.[3] The geometry around the As atoms can be described as distorted tetrahedral with the C–As–O and O–As–O angles significantly narrower than the ideal tetrahedral value. There is a substantial expansion of the As–O–As angles.

Experimental

All manipulations except the preparation of the diarsonic acid (5) were carried out under an atmosphere of prepurified, dry nitrogen. Solvents were dried and purified prior to use by conventional methods. Chemicals of the best available commercial grade were used, in general without further purification. The melting points were determined in sealed capillaries and are uncorrected.

Physical Measurements.—The i.r. spectra were measured with Zeiss model IMR 16, IMR 25, and Perkin-Elmer model 577 instruments and are accurate to ±3 cm^{-1}. Raman spectra were recorded on a Cary 82 laser Raman spectrometer (Varian) equipped with a Kr^+ (exciting line, 647.1 nm) or an Ar^+ laser (exciting line, 514.5 nm) from Spectra Physics. JEOL JNM-PX 60 and JNM-PS 100 spectrometers were used to obtain the ^1H n.m.r. spectra. The spectra were simulated using a Nicolet-1080 computer (standard software, NMR-CAL). Field desorption (f.d.) and election impact (e.i.) mass spectra were measured with a Varian MAT 212 instrument [e.i.: IXE-5 source, 70 eV (*ca.* 1.1 × 10^{-17} J), direct inlet method]. Differential thermal analyses were carried out using a Netzsch

Table 2. Bond lengths (Å) and angles (°) for $(CH_2)_3As_4O_4(CH_2)_3$ (**4**) with estimated standard deviations in parentheses

As(1)–O(1)	1.773(6)	As(3)–C(4)	1.987(9)
As(1)–O(4)	1.796(6)	As(4)–O(3)	1.794(6)
As(1)–C(1)	1.950(9)	As(4)–O(4)	1.802(5)
As(2)–O(1)	1.804(6)	As(4)–C(6)	1.970(9)
As(2)–O(2)	1.811(6)	C(1)–C(2)	1.490(13)
As(2)–C(3)	1.939(8)	C(2)–C(3)	1.521(14)
As(3)–O(2)	1.785(5)	C(4)–C(5)	1.515(13)
As(3)–O(3)	1.791(6)	C(5)–C(6)	1.502(14)
O(1)–As(1)–O(4)	101.8(3)	O(4)–As(4)–C(6)	93.1(3)
O(1)–As(1)–C(1)	98.9(3)	As(1)–O(1)–As(2)	129.4(3)
O(4)–As(1)–C(1)	92.1(3)	As(2)–O(2)–As(3)	123.2(3)
O(1)–As(2)–O(2)	99.9(3)	As(3)–O(3)–As(4)	129.1(3)
O(1)–As(2)–C(3)	101.6(4)	As(1)–O(4)–As(4)	121.8(3)
O(2)–As(2)–C(3)	92.5(3)	As(1)–C(1)–C(2)	114.5(6)
O(2)–As(3)–O(3)	103.1(3)	C(1)–C(2)–C(3)	114.2(8)
O(2)–As(3)–C(4)	92.3(3)	As(2)–C(3)–C(2)	116.5(6)
O(3)–As(3)–C(4)	99.0(3)	As(3)–C(4)–C(5)	113.6(6)
O(3)–As(4)–O(4)	100.5(3)	C(4)–C(5)–C(6)	115.2(7)
O(3)–As(4)–C(6)	101.1(4)	As(4)–C(6)–C(5)	115.8(6)

Table 3. Atomic co-ordinates for the non-hydrogen atoms of $(CH_2)_3As_4O_4(CH_2)_3$ (**4**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
As(1)	−0.011 6(1)	−0.797 98(6)	−0.335 81(8)
As(2)	0.431 1(1)	−0.784 01(6)	−0.410 40(7)
As(3)	0.563 5(1)	−0.897 15(7)	−0.186 24(7)
As(4)	0.115 2(1)	−0.927 42(7)	−0.128 01(7)
O(1)	0.220 9(9)	−0.746 6(4)	−0.339 0(5)
O(2)	0.479 6(9)	−0.890 3(4)	−0.335 5(5)
O(3)	0.348 8(8)	−0.873 1(4)	−0.113 1(5)
O(4)	0.050 4(9)	−0.908 7(4)	−0.279 8(5)
C(1)	−0.040(1)	−0.843 0(6)	−0.494 5(8)
C(2)	0.127(1)	−0.898 6(6)	−0.529 1(7)
C(3)	0.311(1)	−0.844 3(6)	−0.546 2(7)
C(4)	0.549(1)	−1.031 8(6)	−0.186 7(7)
C(5)	0.353(1)	−1.068 4(6)	−0.231 5(7)
C(6)	0.191(2)	−1.054 4(6)	−0.152 8(7)

STA 429 (Selb West Germany) instrument. Potentiometric titration data were obtained with a Beckman 3500 digital pH-meter. Conductivity measurements were carried out using a LF 39 instrument (Weilheim, Technische Werkstätten, West Germany).

Preparation.—1,3-Bis(diphenylarsino)propane, (**1**),[13] was prepared following the method of Hewertson and Watson[22] from $As(C_6H_5)_3$,[23] sodium, and 1,3-dichloropropane in liquid ammonia. Colourless crystals of (**1**) were obtained in good yield (70%),[14] m.p. 67—69 °C (lit.,[13] 70—71 °C) (Found: C, 64.90; H, 5.30%; M^+, 500. $C_{27}H_{26}As_2$ requires C, 64.80; H, 5.25%; *M*, 500). Mass spectrum (e.i., direct inlet, 100 °C), *m/z* 500 (relative intensity 10%, M^+), 423 (100, $M - C_6H_5$), 229 [36, $As(C_6H_5)_2$], and 227 [36, $As(C_6H_4)_2$]. δ_H (60 MHz, solvent $CDCl_3$, standard $SiMe_4$), 1.7 (2 H, m, $C\text{–}CH_2\text{–}C$), 2.0 (4 H, m, $CH_2\text{–}As$), and 7.25 (20 H, m, C_6H_5). I.r.:[14] $\nu(As\text{–}CH_2)$ at 575w–m cm^{-1} (KBr). Raman:[14] $\nu(As\text{–}CH_2)$ at 578w–m and 526w cm^{-1} (pure solid compound).

1,3-*Bis*(*di-iodoarsino*)*propane*, (**2**). The diarsine (**1**) (33.0 g, 65.9 mmol) was dissolved in CH_2Cl_2 (500 cm^3) and a stream of gaseous, dry (4Å molecular sieve) HI[2,15] was bubbled through the solution at room temperature for 9 h. Pale yellow needles of (**2**) precipitated within 48 h. These were filtered off, washed with CCl_4 (4 × 20 cm^3), and dried *in vacuo* (35.2 g, 76.2%), m.p. 37—39 °C. $I_2As(CH_2)_3AsI_2$ (**2**) is readily soluble in thf and CS_2 and slightly soluble in CH_2Cl_2 and diethyl ether. The molar conductivity of a 1.8 × 10^{-4} mol dm^{-3} solution in thf (23 °C) is 24.2 S cm^2 mol^{-1} (Found: C, 5.20; H, 0.95. $C_3H_6As_2I_4$ requires C, 5.15; H, 0.95%; *M*, 700.) Mass spectrum (e.i., direct inlet, 130 °C), *m/z* 573 (relative intensity 31%, $M^+ - I$), 531 (3, As_2I_3), 446 (17, $M - I_2$), 404 (7, As_2I_2), 329 (12, AsI_2), 319 (100, $M - 3I$), 277 (26, As_2I), 254 (15, I_2), 202 (15, AsI), and 127 (19, I). δ_H (60 MHz, solvent CS_2, standard $SiMe_4$), 2.2 (2 H, m, $C\text{–}CH_2\text{–}C$) and 2.9 (4 H, m, $CH_2\text{–}As$).

1,2-*Di-iodo*-1,2-*diarsacyclopentane*, (**3**). Sodium sand (1.5 g, 65.2 mmol) was added to a quickly stirred solution of 1,3-bis(di-iodoarsino)propane (**2**) (3.30 g, 4.71 mmol) in thf (40 cm^3). The suspension was warmed to 60—70 °C until the reaction had started, and the liberated heat of reaction was adjusted so that the thf just refluxed. The colour of the solution changed from red *via* dark green to yellow. After cooling the reaction mixture to room temperature, NaI and the unreacted sodium were filtered off. The solvent was removed under reduced pressure and the resulting brown residue was extracted with CS_2 (20 cm^3). The volume of the extract was reduced to 5 cm^3 and diethyl ether (30 cm^3) was added. The mixture was maintained at *ca.* −20 °C for 2 d, thereby affording a red-brown product. This was filtered off, recrystallized from $CS_2\text{–}CH_2Cl_2$ (5 cm^3, 10 cm^3) and the resulting carmine-red, microcrystalline complex (**3**) was dried *in vacuo* (1 327 mg, 63.0%). Leaving to stand in daylight (7 d), the red modification of (**3**) was converted into the stable brown form, which melted with red colouration at 140—142 °C. The brown form of (**3**) can be transformed again into the red modification by dissolving in CS_2 and evaporation of the solvent under reduced pressure. The dimorphism of (**3**) was also confirmed by differential thermal analysis, which showed two endothermic transformations (125 °C: red modification $\longrightarrow$ brown form; 138 °C: brown form $\longrightarrow$ red colouration with melting). The molar conductivity of a 3.14 × 10^{-4} mol dm^{-3} solution in thf (23 °C) was 11.6 S cm^2 mol^{-1} (Found: C, 8.30; H, 1.35%; M^+, 446. $C_3H_6As_2I_2$ requires C, 8.10; H, 1.35%; *M*, 445.7). Mass spectrum (e.i., direct inlet, 23 °C), *m/z* 446 (relative intensity 12%, M^+), 404 (41, As_2I_2), 319 (100, $M - I$), 277 (65, As_2I), 202 (8, AsI), 128 (4, HI), and 127 (4, I); f.d. (brown modification, 3 kV, 23 °C), *m/z* 446 (M^+). δ_H (100 MHz, solvent CS_2, standard $SiMe_4$), 2.7 (m, CH_2).

2,8,13,14-*Tetraoxa*-1,3,7,9-*tetra-arsatricyclo*[7.3.1.1^{3,7}]*tetradecane*, (**4**). A solution of concentrated aqueous ammonia (30%, *ca.* 5 cm^3) was added dropwise to a stirred solution of 1,3-bis(di-iodoarsino)propane, (**2**) (3.30 g, 4.71 mmol), in hot (60 °C) thf (20 cm^3) until the original reddish orange solution became colourless. The solvent was removed under reduced pressure and the residue dissolved in boiling water (30 cm^3). The solvent was allowed to evaporate at room temperature. After 3 d colourless, prismatic crystals of (**4**) were collected by suction, washed twice with cold water (2 × 2 cm^3), and dried *in vacuo* (640 mg, 30.3%), m.p. > 300 °C. $(CH_2)_3As_4O_4(CH_2)_3$ (**4**) is very soluble in thf, methanol, and CS_2, moderately soluble in diethyl ether, and slightly soluble in aliphatic hydrocarbons. It is also soluble in hot water and recrystallizes unchanged as shown by i.r., mass, and ^1H n.m.r. spectroscopy. For the crystal-structure determination compound (**4**) was recrystallized from methanol–diethyl ether (1:5). **CAUTION**: Compound (**4**) must be handled with the greatest care, and use of a very efficient hood is necessary. Contact must be avoided with either the solid or the vapour. Protective clothes and gloves are also necessary [compound (**4**) and its vapour irritate the skin and the mucous membranes very severely] (Found: C, 16.30; H, 2.95%; M^+, 448. $C_6H_{12}As_4O_4$ requires C, 16.10; H, 2.70%; *M*, 447.8). Mass spectrum (e.i., direct inlet, 80 °C), *m/z* 448 (relative intensity

100%, M^+), 406 (52, $M - C_3H_6$), 364 (82, As_4O_4), 315 [52, $(CH_2)_3As_3O_3$], 273 (51, As_3O_3), and 257 (28, As_3O_2). δ_H (100 MHz, solvent CS_2, standard $SiMe_4$), 1.6 (10 H, m) and 3.1 (2 H, m); (solvent D_2O, external standard Me_2SO), 1.95 (m); (solvent D_2O–KOH, *ca.* 20%, external Me_2SO), 1.8 (m).

Propane-1,3-*bis*(*arsonic acid*), (**5**). This compound was prepared following earlier published procedures[7] from H_2O_2 (1 cm^3, 30%, 8.82 mmol) and 1,3-bis(di-iodoarsino)propane, (**2**) (1.82 g, 2.60 mmol), in dichloromethane (20 cm^3). Recrystallization of $(HO)_2OAs(CH_2)_3AsO(OH)_2$ (**5**) from hot water (30 cm^3) yielded colourless plates (626 mg, 82.5%), m.p. 182—185 °C. The molar conductivity of a 4.91×10^{-4} mol dm^{-3} solution in H_2O (23 °C) was 162 S cm^2 mol^{-1} (Found: C, 12.30; H, 3.55. $C_3H_{10}As_2O_6$ requires C, 12.35; H, 3.45%; *M*, 291.9). Mass spectrum (e.i., direct inlet, 160 °C), *m*/*z* 396 (100%, As_4O_6), 291 (1, $M - H$), 289 (47, As_3O_4), and 240 (14, $C_3H_6As_2O_3$). δ_H (solvent D_2O, external standard Me_2SO), 2.3 (2 H, m, C–CH_2–C), 2.7 (4 H, m, CH_2As), and 4.8 [s, AsOH and H_2O from D_2O (99.5%)].

Crystal-structure Determination of $(CH_2)_3As_4O_4(CH_2)_3$ (**4**).—*Crystal data.* $C_6H_{12}As_4O_4$, $M = 447.85$, monoclinic, space group $P2_1/c$ (no. 14), $a = 6.886(2)$, $b = 14.745(5)$, $c = 11.577(4)$ Å, $\beta = 94.15(3)°$, $U = 1\,172.3$ Å^3, $Z = 4$, $D_c = 2.537$ g cm^{-3}, $F(000) = 848$, $\mu(Mo\text{-}K_\alpha) = 112.7$ cm^{-1}.

Data collection. A single crystal of approximate dimensions $0.2 \times 0.2 \times 0.3$ mm was chosen for the *X*-ray investigation. The systematic absences observed suggested the space group to be $P2_1/c$. The lattice constants were determined accurately using an Enraf-Nonius CAD-4 automated single-crystal diffractometer [Mo-K_α radiation ($\lambda = 0.71073$ Å), graphite monochromator] with 25 precisely centred high-angle reflections. For the structure determination 4 183 intensities were measured, with an ω/θ scan in the θ range 3—28°. After averaging the equivalent reflections of the reciprocal lattice, there remained 2 026 reflections with intensities $I \geqslant 3\sigma(I)$. Intensity data were corrected for Lorentz and polarization effects and absorption.[24]

Solution and refinement of the structure.[25] The positions of the four As atoms were found by direct methods (MULTAN[26]) and Fourier-difference syntheses were used to locate the remaining non-hydrogen atoms. After isotropic refinement of all the non-hydrogen atoms ($R = 0.144$), the DIFABS method of absorption correction[24] was applied. Refinement using anisotropic thermal parameters for all atoms gave an *R* factor of 0.043. Including the calculated H-atom positions in the structure factor calculations led to a final *R* value of 0.038 ($R' = 0.045$). Atomic co-ordinates for the non-hydrogen atoms (with estimated standard deviations) are given in Table 3.

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