

Oxidation of $(\text{AsPh}_2)_2\text{E}$ ($\text{E} = \text{O}$ or S); supramolecular hydrogen-bonded self-assembly of an unusual tetranuclear adduct and crystal structure of $[\text{AsPh}_2(\text{O})\text{OH} \cdot \text{AsPh}_2(\text{S})\text{OH}]_2$

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Abstract

Oxidation of $(\text{AsPh}_2)_2\text{E}$ ($\text{E} = \text{O}$ or S) with tert-butyl hydroperoxide and sulfur in the ratios 1 : 1 and 1 : 2 has been investigated in an attempt to produce compounds of the type $\text{AsPh}_2(\text{E})\text{--E--AsPh}_2$ and $[\text{AsPh}_2(\text{E})]_2\text{E}$. Although it has been possible to isolate all four compounds of the type $\text{AsPh}_2(\text{E})\text{--E--AsPh}_2$, where $\text{E} = \text{O}$ or S , the dioxidation products are less stable and recrystallisation of the products from oxidation of $(\text{AsPh}_2)_2\text{O}$ with sulfur and $(\text{AsPh}_2)_2\text{S}$ with tert-butyl hydroperoxide leads to a mixed arsenic acid–monothioarsinic acid $[\text{AsPh}_2(\text{O})\text{OH} \cdot \text{AsPh}_2(\text{S})\text{OH}]_2$. This compound has an unusual tetranuclear structure, arising from simultaneous intermolecular hydrogen bond formation between the OH groups of the constituent acids and the oxygen of a centrosymmetrically related diphenylarsinic acid molecule.

Keywords: Arsenic; Crystal structure; Hydrogen bonding; Arsinic acid; Thioarsinic acid

1. Introduction

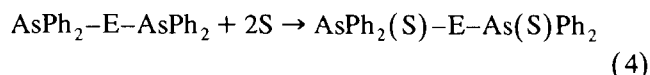
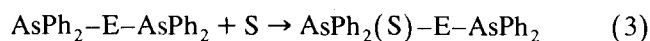
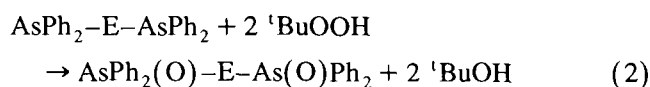
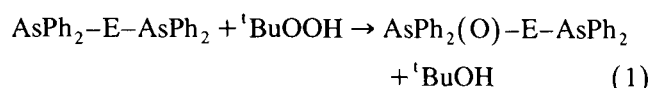
Although arsenic acids $\text{AsR}_2(\text{O})(\text{OH})$ and their thio analogs $\text{AsR}_2(\text{S})(\text{SH})$ are readily available and well known compounds [1,2], little is known about the corresponding anhydrides **1** and **2**. Such compounds are, however, interesting as potential chelating ligands and for comparison of their reactivity with those of the better known phosphorus analogs and the ethylene bridged bis(arsenic) oxides and sulfides **3** ($\text{X} = \text{O}$ or S) [3,4]. The work reported in this paper deals with attempts to produce such compounds by oxidation of bis(diphenylarsenic) oxide and sulfide with both tert-butyl hydroperoxide and elemental sulfur.

2. Results and discussion

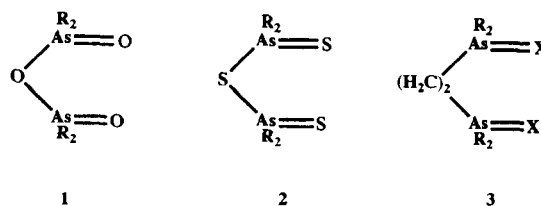
2.1. Preparations

The following equations ($\text{E} = \text{O}$ or S) can be written for the reactions investigated which, depending on the

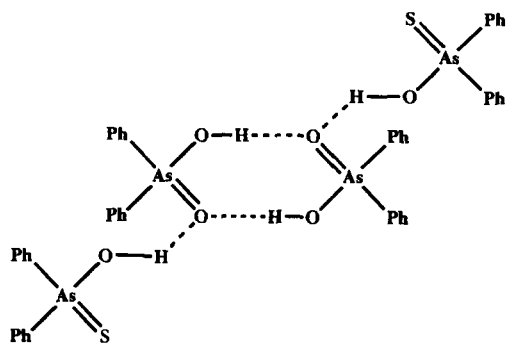
molar ratio of reagents, were expected to yield mono- and dioxo and thio compounds.



All four potential mono-oxidation products $\text{AsPh}_2(\text{S})\text{--E--AsPh}_2$ and $\text{AsPh}_2(\text{O})\text{--E--AsPh}_2$, where



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E = O or S, have been obtained as outlined in Eqs. (1) and (3) above, by treating the arsenic oxide and sulfide with 1 mol of either tert-butyl hydroperoxide or elemental sulfur. The compounds, which are white solids, have been identified by conventional analysis and IR spectroscopy and, with the exception of $\text{AsPh}_2(\text{S})\text{O}-\text{AsPh}_2$, can be recrystallised in the open laboratory. With $\text{AsPh}_2(\text{S})\text{O}-\text{AsPh}_2$, recrystallisation under these conditions leads to hydrolysis and isolation of compound **4**, later identified as a novel mixed arsenic acid-monothioarsinic acid.

The corresponding dioxidation products [see Eqs. (2) and (4)] are apparently hydrolytically much less stable and, although it was possible to obtain $\text{AsPh}_2(\text{O})\text{O}-\text{As}(\text{O})\text{Ph}_2$ from a reaction of $(\text{AsPh}_2)_2\text{O}$ with 2 mol of tert-butyl hydroperoxide, it was always accompanied by its hydrolysis product, diphenylarsinic acid. Indeed, it is probably only possible to recrystallise the bis(arsenic) dioxide intact if moisture is completely excluded. There was no evidence for $\text{AsPh}_2(\text{O})\text{S}-\text{As}(\text{O})\text{Ph}_2$ from the corresponding reaction with $(\text{AsPh}_2)_2\text{S}$, nor for $\text{AsPh}_2(\text{S})\text{O}-\text{As}(\text{S})\text{Ph}_2$ from the reaction of $(\text{AsPh}_2)_2\text{O}$ and sulfur; in each case the only product isolated was compound **4**. The ubiquitous nature of compound **4**, which is a white crystalline solid melting at 146°C , is shown too by the fact that it also resulted when

$(\text{AsPh}_2)_2\text{S}$ itself was recrystallised from acetonitrile in the open laboratory. There is clearly a high driving force for formation of this species, pointing to its great stability. Finally, an attempt to oxidize $(\text{AsPh}_2)_2\text{S}$ with 2 mol of sulfur gave an unidentified oil.

2.2. Infrared spectroscopy

Important bands in the infrared spectra of these compounds are summarized in Table 1, and to aid in their assignment PM3 frequency calculations have been carried out using the SPARTAN 4.0 molecular modelling package [5a]. The symmetric and antisymmetric As–O–As stretching modes in $(\text{AsPh}_2)_2\text{O}$ are assigned at 555 and 765 cm^{-1} respectively, close to the values calculated for both $(\text{AsPh}_2)_2\text{O}$ and its methyl analog [5b]. The similarity in positions for these two bands, and the form of the corresponding normal modes, show that there is no coupling with other normal modes and that these frequencies are indeed due to vibrations well localised on the As–O–As bridge. The symmetric stretch at 555 cm^{-1} , which occurs in an otherwise clear region of the spectrum, is an excellent correlation for the presence of an As–O–As bridge. As shown in Table 1, band positions associated with this system change little in the mono-oxidation products, but when both arsenic atoms are oxidized, the antisymmetric mode is raised in energy to 880 to 915 cm^{-1} , although there is little change in the corresponding symmetric stretch. As–S–As stretching modes are assigned to medium intensity bands at 392 and 394 cm^{-1} in the spectra of $(\text{AsPh}_2)_2\text{S}$ and $\text{AsPh}_2(\text{S})\text{S}-\text{AsPh}_2$ respectively, and further bands between 478 and 512 cm^{-1} to As=S stretching modes. Calculations show that the relatively high energy for this band in $\text{AsPh}_2(\text{S})\text{O}-\text{SAsPh}_2$ can be ascribed to coupling with the As–O–As stretching mode.

The diphenylarsinic acid spectrum, in addition to a broad band at 2330 cm^{-1} due to $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonding, shows strong bands at 875 , 770 and 755 cm^{-1} due to As–O stretching; the splitting is ascribed to the

Table 1
Selected infrared bands (cm^{-1})

Compound	$\nu_s(\text{As}-\text{O}-\text{As})$	$\nu_{as}(\text{As}-\text{O}-\text{As})$	$\nu(\text{As}-\text{S}-\text{As})$	$\nu(\text{As}=\text{O})$	$\nu(\text{As}=\text{S})$
$(\text{AsPh}_2)_2\text{O}$	555 m	740 s			
$(\text{AsPh}_2)_2\text{S}$			392 m		
$\text{AsPh}_2(\text{S})\text{OAsPh}_2$	552 m	737 s			482 s
$\text{AsPh}_2(\text{S})\text{SAsPh}_2$			394 m		480 m
$\text{AsPh}_2(\text{O})\text{OAsPh}_2$	551 m	750 s		892 s	
$\text{AsPh}_2(\text{O})\text{SAsPh}_2$			390 m	880 s	
$[\text{AsPh}_2(\text{O})]_2\text{O}$	530 m	881 s		912 s	
$[\text{AsPh}_2(\text{S})]_2\text{O}$	560 m	881 s			512 s
$\text{AsPh}_2(\text{O})\text{OH}$				875 s (755 s, 770 s)	
$\text{AsPh}_2(\text{S})\text{OH}$					478
$[\text{AsPh}_2(\text{O})\text{OH} \cdot \text{AsPh}_2(\text{S})\text{OH}]_2$				890 s (745 s, 755 s, 770 m)	510 s

effect of hydrogen bonding. Compound **4** also shows a strong broad absorption at ca. 2400 cm^{-1} and As–O bands at 890 , 770 , 755 and 745 cm^{-1} similar to those in the diphenylarsinic acid spectrum. There is a further band at 510 cm^{-1} , possibly associated with As=S stretching, allowing compound **4** to be identified as some kind of arsenic acid derivative. To identify it completely, its structure has been determined by X-ray crystallography.

2.3. Structure of $\text{AsPh}_2(\text{O})\text{OH} \cdot \text{AsPh}_2(\text{S})\text{OH}_2$ (**4**)

The structure determination shows that compound **4** is an unusual centrosymmetric, hydrogen-bonded, tetranuclear species with overall formula $[\text{AsPh}_2(\text{O})\text{OH} \cdot \text{AsPh}_2(\text{S})\text{OH}]_2$. A diagram showing the molecular structure and atom numbering scheme is given in Fig. 1, and important bond distances and angles are listed in Table 2. The best description of the structure is that of a central dimeric unit containing two hydrogen-bonded diphenylarsinic acid molecules, attached to which are two diphenylmonothioarsinic acid molecules. Hydrogen bonding involves only the As=O units of the diphenylarsinic acid molecules, which participate in bifurcated hydrogen bonding with OH groups of both the diphenylmonothioarsinic acid molecule and the centrosymmetrically related diphenylarsinic acid.

Each arsenic atom has distorted tetrahedral geometry with angles ranging between 102.9 and 113.0° for the arsenic acid and 100.5 and 114.9° for the thioarsinic acid molecule. Angles in the arsenic acid molecule are generally a little larger than in the free acid, and the As–O separations [$1.661(3)$ and $1.724(3)\text{ \AA}$] are longer than those in diphenylarsinic acid itself [$1.639(2)$ and $1.713(2)\text{ \AA}$] [6]. Unfortunately, although diphenyl-

Table 2
Selected bond lengths (\AA) and angles (deg)

As(1)–O(2)	1.661(3)
As(1)–O(1)	1.724(3)
As(1)–C(21)	1.907(5)
As(1)–C(11)	1.908(5)
As(2)–O(3)	1.750(3)
As(2)–C(41)	1.908(6)
As(2)–C(31)	1.929(5)
As(2)–S(1)	2.061(2)
O(1)–O(2A)	2.591(5)
O(2)–O(3)	2.646(5)
O(2)–As(1)–O(1)	113.0(2)
O(2)–As(1)–C(21)	111.0(2)
O(1)–As(1)–C(21)	102.9(2)
O(2)–As(1)–C(11)	112.0(2)
O(1)–As(1)–C(11)	106.6(2)
C(21)–As(1)–C(11)	111.0(2)
O(3)–As(2)–C(41)	100.5(2)
O(3)–As(2)–C(31)	102.6(2)
C(41)–As(2)–C(31)	108.4(2)
O(3)–As(2)–S(1)	114.90(14)
C(41)–As(2)–S(1)	114.4(2)
C(31)–As(2)–S(1)	114.5(2)
As(1)–O(1)–O(2A)	117.4(2)
As(1)–O(2)–O(1A)	126.4(2)
As(1)–O(2)–O(3)	135.1(2)
As(2)–O(3)–O(2)	122.0(2)

Symmetry transformations used to generate equivalent atoms: (A) $1 - x, -y, 1 - z$.

monothioarsinic acid is known [7], structures are not known for any mono- or dithioarsinic acid, and further direct comparisons are not possible. The dithioarsinic acid moiety, however, clearly contains a double-bonded sulfur atom [As–S $2.061(2)\text{ \AA}$] and an As–OH group [As–O $1.750(3)\text{ \AA}$]; the former can be compared with As–S distances in AsPh_3S (mean 2.090 \AA) [8] and

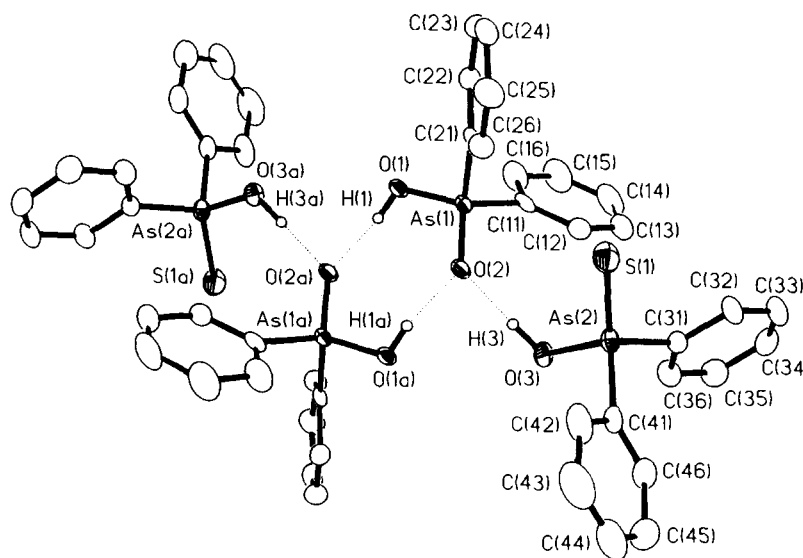
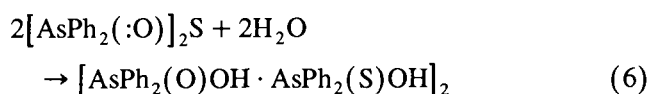
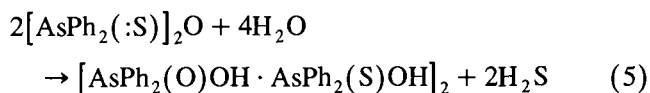


Fig. 1. Molecular structure and atom labelling scheme for $[\text{AsPh}_2(\text{O})\text{OH} \cdot \text{AsPh}_2(\text{S})\text{OH}]_2$.

tri(*p*-chlorophenyl)arsenic (2.074 Å) [9]. The As–O separation is longer than in the arsenic acid component from incorporation of the lower electron-withdrawing sulfur atom. In $\text{AsMe}_2(\text{S})\text{–O–As}(\text{S})\text{Me}_2$, the As=S bonds are 2.067 and 2.077 Å while the bridging As–O distance is 1.786 Å [10].

As the arsenate oxygen is involved in a bifurcated hydrogen bond system, the two $\text{O}\cdots\text{O}$ separations [2.591(5) and 2.646(5) Å] are slightly longer than those in dimethyl (2.57 Å) [11], dibutyl (2.47 Å) [12], divinyl (2.53 Å) [13] and diphenyl (2.522 Å) [6] arsenic acids. Hydrogen bonding would also be expected between the OH group and sulfur atom in monothioarsinates, but none has yet been described; such bonds are however found in monothiophosphinic acid structures where the $\text{O}\cdots\text{S}$ separations (ca. 3.13 Å) are substantially longer and weaker [14,15]. Greater thermodynamic stability is therefore gained when hydrogen bonding is restricted to oxygen systems and it is probably this, coupled with the hydrolytic instability of the primary products [see Eqs. (5) and (6)], that leads to the isolation of compound **4** from both oxidation reactions. The compound is then formed by self-assembly and, following Lehn's definition [16], can be described as supramolecular.



Hydrogen bonding is a frequent constructive principle in the formation of supramolecular structures, not only in biological systems but also in simpler organic and organometallic compounds, and plays an important role in "crystal engineering" [17]. It promotes self-organised associations in compounds, such as carboxylic acids, phosphinic, thiophosphinic and arsenic acids, etc., leading to intermolecular assemblies as entities in crystal packing. Thus centrosymmetric dimers are found for a range of carboxylic acids [18], dimethyl- [11] and dibutyl- [12] arsenic acids and dimethyl- [14] and di(cyclo-hexyl)- [14] monothiophosphinic acids, while an alternative infinite helical chain structure occurs in the solid state structures of formic [19] and acetic [20] acids, diphenyl-phosphinic [21], -monothiophosphinic [15] and -dithiophosphinic [22] acids and divinyl- [13] and diphenyl- [6] arsenic acids. This work now shows that there is a third possibility, based on a centrosymmetric tetranuclear structure.

3. Experimental section

Bis(diphenylarsenic)oxide and the corresponding sulfide were prepared by literature methods [23,24] and all

reactions were carried out under nitrogen in solvents dried by conventional methods. Mass spectra (EI, 70 eV) were obtained for these starting materials. $[(\text{AsPh}_2)_2\text{O}]$, m/z (%) 474 (100) $\text{As}_2\text{Ph}_4\text{O}$, 245 (3) AsPh_2O , 152 (10) AsPh ; $[(\text{AsPh}_2)_2\text{S}]$, m/z (%) 490 (38) $\text{As}_2\text{Ph}_4\text{S}$, 261 (70) AsPh_2S , 184 (17) AsPhS , 152 (61) AsPh , 107 (6) AsS .

3.1. Oxidation of $(\text{AsPh}_2)_2\text{S}$ with ${}^t\text{BuOOH}$

A solution of bis(diphenylarsenic)sulfide (2.45 g, 5 mmol) in dichloromethane (25 ml) was treated with tert-butyl hydroperoxide (3 M in iso-octane 3.33 ml, 10 mmol) at room temperature under nitrogen. After stirring for 1 h, the solvent was slowly evaporated under vacuum to give white crystals of **4** (Yield 88%, melting point 146°C). Anal. Found: C, 53.1, H, 4.1; $\text{C}_{24}\text{H}_{22}\text{As}_2\text{O}_3\text{S}$ Calc.: C, 53.3, H, 4.1%. MS (EI, 70 eV) m/z (%) 490 (6) $\text{As}_2\text{Ph}_4\text{S}$, 474 (32) $\text{As}_2\text{Ph}_4\text{O}$, 397 (12) $\text{As}_2\text{Ph}_3\text{O}$, 278 (8) AsPh_2SOH , 263 (2) $\text{AsPh}_2\text{O}_2\text{H}_2$, 262 (3) $\text{AsPh}_2\text{O}_2\text{H}$, 261 (15) AsPh_2S , 246 (11) AsPh_2OH , 245 (4) AsPh_2O , 243 (2) $\text{AsPh}_2\text{O}(-2\text{H})$, 184 (7) AsPhS , 169 (37) AsPhOH , 152 (100) AsPh , 107 (7) AsS , 91 (43) AsO .

A similar reaction with 1 mol of ${}^t\text{BuOOH}$, however, gave a white solid, which from its melting point and infrared spectrum was identified as $\text{AsPh}_2\text{As}(\text{O})\text{SAsPh}_2$.

3.2. Oxidation of $(\text{AsPh}_2)_2\text{O}$ with sulfur

Bis(diphenylarsenic) oxide (3.2 g, 8.8 mmol) and sulfur (0.44 g, 13.7 mmol) were melted together in a vacuum and stirred for 1 h, after which toluene (30 ml) was added and the solution refluxed for a further 2 h. Evaporation of the solvent gave white crystals of **4**, melting at 146°C. Anal. Found: C, 53.4; H, 4.1%.

Under the same conditions as above, a mixture of $(\text{AsPh}_2)_2\text{O}$ (1.8 g, 3.6 mmol) and sulfur (0.12 g, 3.6 mmol) gave pale yellow crystals of $\text{AsPh}_2(\text{S})\text{OAsPh}_2$, melting at 88°C. Anal. Found: C, 56.9; H, 4.0. $\text{C}_{24}\text{H}_{20}\text{As}_2\text{OS}$ Calc.: C, 57.7; H, 4.1%. MS (EI, 70 eV) m/z (%) 490 (38) $\text{As}_2\text{Ph}_4\text{S}$, 263 (6) $\text{AsPh}_2\text{O}_2\text{H}_2$, 262 (6) $\text{AsPh}_2\text{O}_2\text{H}$, 184 (4) AsPhS , 152 (100) AsPh , 107 (6) AsS .

3.3. Oxidation of $(\text{AsPh}_2)_2\text{O}$ with ${}^t\text{BuOOH}$

A solution of bis(diphenylarsenic) oxide (4.7 g, 10 mmol) in dichloromethane (40 ml) was treated at 0°C with an iso-octane solution of tert-butyl hydroperoxide (3 M, 6.7 ml, 20 mmol) and stirred for 1 h. The solvent was removed at room temperature under nitrogen and the residue recrystallised from anhydrous CH_2Cl_2 again under nitrogen to give white crystals (3.1 g, 61.3%) of $[(\text{AsPh}_2(\text{O}))_2]_2\text{O}$. Melting point 158°C. Anal. Found: C,

56.4; H, 4.2. $C_{24}H_{20}As_2O_3$. Calc.: C, 56.9; H, 4.0%. MS (EI, 70 eV) m/z (%) 474 (5) As_2Ph_4O , 429 (17) $As_2Ph_3O_3$, 413 (11) $As_2Ph_3O_2$, 397 (7) As_2Ph_3O , 263 (12) $AsPh_2O_2H_2$, 262 (12) $AsPh_2O_2H$, 261 (48) $AsPh_2O_2$, 246 (15) $AsPh_2OH$, 245 (12) $AsPh_2O$, 243 (20) $AsPh_2O(-2H)$, 169 (41) $AsPhOH$, 152 (39) $AsPh$, 91 (43) AsO .

Further concentration of the filtrate from above gave crystals of diphenylarsinic acid, melting point 173°C. The dioxidized compound $[AsPh_2(O)]_2O$ was also produced when diphenylarsinic acid was heated to 180°C in a vacuum for 24 h.

When the reaction was carried out as described above but using bis(diphenylarsenic) oxide (4.7 g, 10 mmol) and tert-butyl hydroperoxide (3 M, 3.3 ml, 10 mmol), the product was $AsPh_2(O)OAsPh_2$ in almost quantitative yield. Melting point 128°C. Anal. Found: C, 58.2; H, 4.2. $C_{24}H_{20}As_2O_2$. Calc.: C, 58.9; H, 4.1%. MS (EI, 70 eV) m/z (%) 474 (7) As_2Ph_4O , 397 (9) As_2Ph_3O , 263 (16) $AsPh_2O_2H_2$, 261 (1) $AsPh_2O_2$, 246 (2) $AsPh_2OH$, 245 (5) $AsPh_2O$, 243 (2) $AsPh_2O(-2H)$, 169 (7) $AsPhOH$, 152 (100) $AsPh$, 91 (7) AsO .

The same compound was also obtained from a reaction between diphenylarsenic chloride (2.9 g, 10 mmol) and sodium diphenylarsinate (2.8 g, 10 mmol) in benzene (30 ml). After separation of the precipitated sodium chloride, partial evaporation of the solvent gave white crystals of $AsPh_2(O)OAsPh_2$.

3.4. Oxidation of $(AsPh_2)_2S$ with sulfur

A mixture of $(AsPh_2)_2S$ (1.2 g, 2.5 mmol) and sulfur (0.08 g, 2.5 mmol) was held at 90–100°C under vacuum for 1 h, after which the mixture was taken up in toluene and refluxed for a further 1 h. Partial evaporation of the solution and cooling gave white crystals of $AsPh_2(S)SAsPh_2$ (28%), melting at 93°C. The product was contaminated with sulfur which was impossible to remove by recrystallisation. The same compound has been obtained pure from the reaction of diphenylarsenic chloride and sodium diphenyldithioarsinate [25].

Under the same conditions, the reaction of $(AsPh_2)_2S$ with 2 mol of sulfur gave an oil which could not be crystallised.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

Atom	x	y	z	U_{eq}
As(1)	2658(1)	1337(1)	5410(1)	18(1)
O(1)	3274(4)	311(4)	4376(3)	24(1)
O(2)	3871(4)	994(3)	6221(3)	22(1)
C(11)	2275(6)	3053(5)	4467(5)	24(1)
C(12)	2149(6)	4046(5)	4986(6)	35(2)
C(13)	1838(7)	5296(6)	4331(7)	41(2)
C(14)	1645(8)	5548(6)	3164(7)	51(2)
C(15)	1769(8)	4564(7)	2631(6)	50(2)
C(16)	2085(7)	3303(6)	3293(6)	40(2)
C(21)	826(6)	1066(5)	6459(5)	19(1)
C(22)	-289(6)	1193(5)	5940(5)	25(1)
C(23)	-1620(7)	1025(6)	6704(6)	33(1)
C(24)	-1847(7)	718(5)	7960(6)	33(1)
C(25)	-736(7)	596(6)	8483(5)	35(2)
C(26)	596(6)	774(5)	7732(5)	27(1)
As(2)	3235(1)	3188(1)	8442(1)	21(1)
S(1)	1314(2)	2683(2)	9241(2)	40(1)
O(3)	4559(4)	2351(4)	7264(3)	26(1)
C(31)	2887(6)	4975(5)	7635(5)	21(1)
C(32)	1527(6)	5896(5)	8073(5)	31(1)
C(33)	1274(7)	7178(5)	7479(6)	36(2)
C(34)	2336(7)	7524(6)	6473(5)	33(2)
C(35)	3688(7)	6612(6)	6049(5)	34(2)
C(36)	3967(7)	5326(5)	6625(5)	30(1)
C(41)	4440(6)	2790(5)	9539(5)	24(1)
C(42)	4468(8)	1696(6)	10476(5)	40(2)
C(43)	5413(9)	1350(7)	11231(6)	54(2)
C(44)	6248(9)	2093(7)	11098(7)	58(2)
C(45)	6249(8)	3167(7)	10186(7)	52(2)
C(46)	5324(7)	3524(5)	9392(6)	37(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

3.5. Crystal structure of 4

3.5.1. Crystal data

$C_{24}H_{22}As_2O_4S$, $M = 540.4$, $T = 154$ K, triclinic, space group $P1$, $a = 10.057(3)$, $b = 11.471(5)$, $c = 11.736(2)$ Å, $\alpha = 72.69(3)$, $\beta = 69.32(3)$, $\gamma = 66.22(2)^\circ$; $U = 1139.9(5)$ Å³, $Z = 2$, $D_c = 1.574$ g cm⁻³, $F(000) = 544$, $\mu = 30.46$ cm⁻¹, Mo K α radiation, $\lambda = 0.710$ 73 Å, crystal size $0.15 \times 0.15 \times 0.20$ mm³.

3.5.2. Structure determination

Intensities for 4893 reflections ($-10 < h < 11$, $-13 < k < 13$, $-12 < l < 13$, 3197 independent reflections $R_{int} = 0.0976$) were measured at low temperature using a Delft Instruments FAST TV area detector diffractometer situated at the window of a rotating molybdenum anode generator operating at 50 kV and 45 mA. The structure was solved by direct methods (SHELXS-86) [26] and refined using all data (full-matrix least-squares methods on F^2) using the SHELXL-93 programs [27]. All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms of the phenyl groups were placed in calculated positions and treated as riding atoms. The two hydroxo protons were identified from a Fourier difference synthesis but were again treated as riding atoms. Refinement converged (272 parameters) at $wR_2(F^2) = 0.171$ (goodness of fit 1.104), equivalent to a conventional $R(F) = 0.063$ (for 2816 reflections with $I > 2\sigma(I)$). A final Fourier difference synthesis showed the largest peak (2.01 e Å⁻³) in the vicinity of the arsenic atom; the largest hole was -1.12 e Å⁻³. The final atomic coordinates are listed in Table 3. A full listing of bond lengths and angles, hydrogen atom coordinates and thermal parameters has been deposited at the Cambridge Crystallographic Data Centre.

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References and notes

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