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The first oxygen-bridged diorganoarsenic(V) compound: the crystal structure of $AsMe_2(S)OAs(S)Me_2$

Luminita Silaghi-Dumitrescu [a], Sofia Pascu [a], Ioan Silaghi-Dumitrescu [a], Ionel Haiduc [a], Martin N. Gibbons [b], D. Bryan Sowerby [b,*]

[a] *Department of Chemistry, Babes-Bolyai University Cluj-Napoca, Cluj-Napoca RO-3400, Romania*
[b] *Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK*

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Abstract

The oxidation of tetramethyldiarsinedisulfide, $(AsMe_2S)_2$, with *t*-BuOOH under anhydrous conditions leads to both $AsMe_2(S)$–S–$As(O)Me_2$ **1** and $AsMe_2(S)$–O–$As(S)Me_2$ **2**. The formation of the oxygen-bridged isomer **2** is unexpected and can be rationalised as resulting from either oxidation of the As(III)/As(III) form of the disulfide, ($AsMe_2$–S–S–$AsMe_2$), or by an oxotropic rearrangement of **1** via a cyclic As_2OS transition state. RHF/3-21G* ab initio calculations predict that the oxo-bridged species **2** is more stable than the thio-bridged form **1**. The molecular structure of **2** has been determined by single crystal X-ray diffraction. © 1997 Elsevier Science S.A.

Keywords: Oxidation; Diorganoarsenic(V) compound; Tetramethyldiarsinedisulfide

1. Introduction

Although there are many phosphorus(V) compounds which contain the P(*X*)–*Y*–P(*X*) framework, where *X*,*Y* = O or S [1,2], there are no reported examples of the corresponding arsenic analogues. The only similar diarsenic(V) compounds contain -CH_2- or -$(CH_2)_2$- bridges [3–8], but mixed As(III)/As(V) derivatives such as $AsR_2(X)$–*Y*–AsR_2, where *X*,*Y* = O, S, have been investigated to some extent [9–12]. The chemistry of organoarsenic derivatives containing two As(V) atoms connected by a chalcogen atom bridge (O,S) was our concern recently [12,13]; here, we report the results on the oxidation of tetramethyldiarsine disulfide with *t*-butyl hydroperoxide.

2. Results and discussion

2.1. Preparation and ^1H NMR spectroscopy

Oxidation of tetramethyldiarsine disulfide, $AsMe_2(S)SAsMe_2$, with 1 mol of *t*-BuOOH in anhydrous benzene under an inert atmosphere was carried out to obtain an As(V)/As(V) compound containing an As–S–As bridge as shown in the following equation.

$$Me_2As(S) - S - AsMe_2 + tBuOOH \rightarrow Me_2As(=S) - S - AsMe_2(=O)$$

However, the expected oxidation product, $AsMe_2(S)SAs(O)Me_2$ **1**, formed by addition of oxygen to the As(III) centre, was not the only product of the reaction, and an isomer containing an As–O–As bridge, $AsMe_2(S)O(S)AsMe_2$ **2**, was also isolated. Compound **2** crystallised first from a benzene solution, while compound **1** was obtained after concentration of the mother liquor. From elemental analysis and IR and NMR spectroscopy, compound **1** was isolated as the monohydrate. IR and NMR spectra were also recorded for **2**, and its molecular structure was established by X-ray diffraction. A possible pathway for isomerisation of **1** to **2** was sought using molecular orbital calculations. The simultaneous formation of **1** and **2** during the reaction is also taken into consideration in the following discussion.

^1H NMR spectra of $AsMe_2(S)S(O)AsMe_2$ **1** showed signals with the correct relative intensities at 1.90 and 1.98 ppm for the methyl groups attached to the differ-

* Corresponding author.

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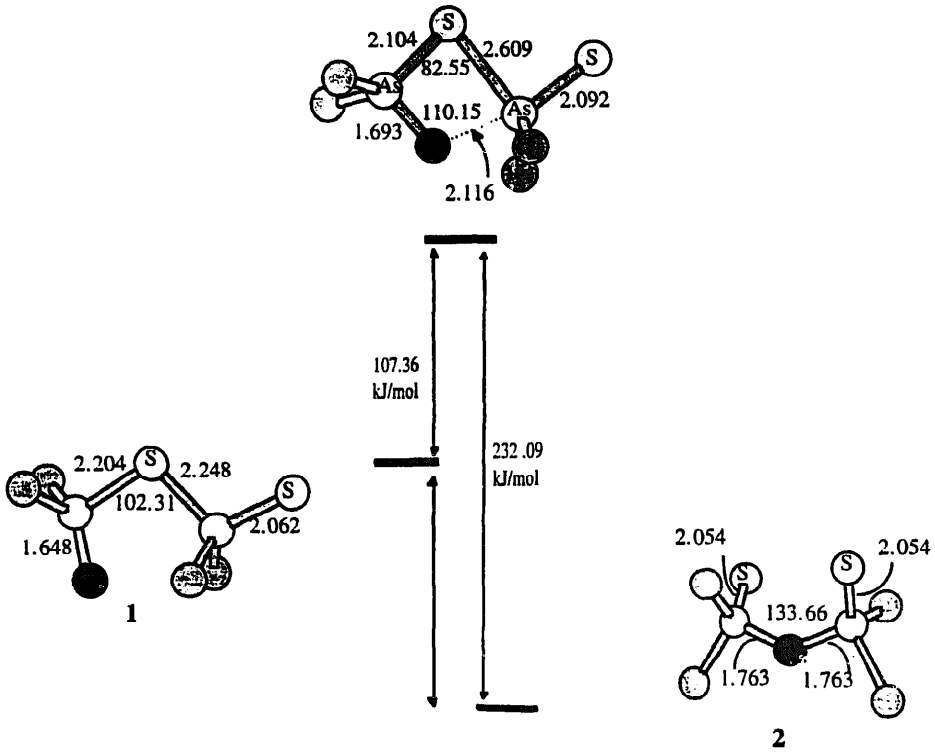

Fig. 1. Calculated structures and relative energies of $AsMe_2(O)SAs(S)Me_2$ **1**, $AsMe_2(S)OAs(S)Me_2$ **2** and of the cyclic transition state connecting **1** and **2**.

ently substituted arsenic atoms and a further signal at 8.24 ppm for the water protons. On the other hand, there was only one signal at 2.22 ppm for the methyl groups in the proton spectrum of **2**. The spectrum of the original reaction mixture contained signals for both **1** and **2**, and no changes were observed in spectra recorded

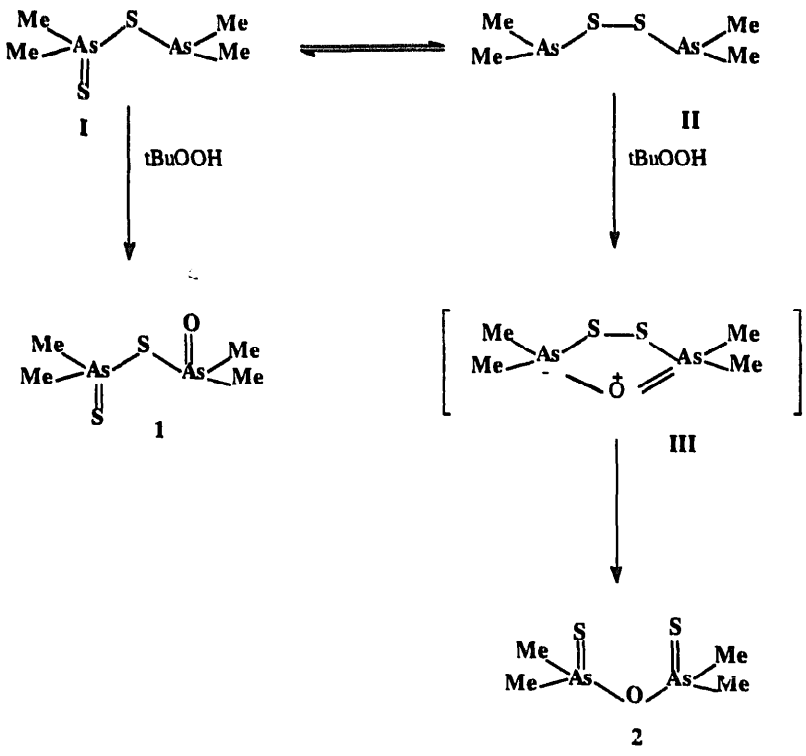

Fig. 2. Two possible pathways for the oxidation of tetramethyldiarsine disulfide. The oxidation of **II** to **III** proceeds faster than that of **I** to **1**.

Table 1
Calculated and experimental skeletal vibrations (cm^{-1}) for $Me_2As(S)SAs(O)Me_2$ **1**

Ab initio	PM3	Experimental	Type of vibration
306	305	393	Symmetric As–S–As stretch + As = S and As = O stretches
434	419	415	As–S–As antisym. stretch
448	425	482	As = S stretch
531	570	610	As–C symmetric stretch + As = S stretch
656	579	635/653	As–C antisymmetric stretch + As = O stretch
981	945	889	As = O stretch

after several days standing at room temperature in the open atmosphere. From these data, it follows that once formed, **2** does not convert into **1** at normal temperatures, and both **1** and **2** can be isolated from the same solution. This finding is surprising, since in similar systems [6,7], molecular rearrangements have been observed on the NMR time scale.

2.2. Molecular orbital calculations

To gain a deeper insight into these systems, PM3 molecular orbital calculations were performed on **1** and **2**, and a possible transition state (TS) connecting them was also located. The structures thus obtained were further optimised within the ab initio module of Spartan (using the TS option for the transition state location) The ab initio calculated relative energies of the optimised TS structure together with those of the two isomers are shown in Fig. 1.

The TS, characterised by only one negative eigenvalue of the force constant matrix, is ca. 107.36 kJ/mol higher in energy than **1** and 232.09 kJ/mol higher than **2**. The barrier separating **1** and **2** support the NMR data and suggests that rearrangement of **1** to **2** including the cyclic TS structure is rather improbable. These data also suggest that formation of the oxo-bridged isomer **2** is controlled thermodynamically, while the sulfur-bridged isomer **1** is the kinetically favoured product. Since an oxotropic rearrangement is unlikely, due to the relatively high barrier, it is reasonable to suggest that both **1** and **2** are formed directly during the oxidation of tetramethyldiarsinedisulfide, and possible reaction pathways are shown schematically in Fig. 2.

It has been shown [9,10] that disulfides, $(AsR_2S)_2$, exist in solution as an equilibrium mixture of $AsR_2(S)$–S–AsR_2 **I** and AsR_2–S–S–AsR_2 **II** (see Fig. 2). This equilibrium is shifted towards **II** at higher temperatures, while at low temperatures the As(III)/As(V) form **I** is dominant, and this is the solid state form [14]. In the present experiments ^1H NMR spectra show that **2** is formed in a larger amount than would be expected from the **I**:**II** isomer ratio [9] at the experimental temperature. At 0–5°C when the initial **I**:**II** ratio is greater than 37, i.e., the experimental value at 29.4°C, the corresponding **1**:**2** ratio is reduced to 2.5 and at 40°C, when the concentration of **II** in the initial reaction mixture would be higher, the **1**:**2** ratio falls to 1.44. The present data suggest that **II** is oxidised more rapidly than **I**, and the resulting shift in equilibrium towards **II** may explain why **2** is produced in amounts larger than expected from the **I**:**II** ratio in the absence of the oxidant.

2.3. IR spectroscopy

IR spectra of the two compounds were assigned following literature data [9–11] and, to gain further support, the vibrational modes were evaluated by semiempirical (PM3) and ab initio (RHF/3-21G*) molecular orbital calculations. Tables 1 and 2 summarise the calculated and observed skeletal frequencies for **1** and **2**, respectively, and give approximate descriptions. As a general remark, note that there is considerable mixing of the internal modes, making assignment more ambiguous than for corresponding phosphorus compounds [15] and that the degree of mixing is greater for **2** than for **1**. Thus, in **1**, the 373 cm^{-1} band can be

Table 2
Calculated and experimental skeletal vibrations (cm^{-1}) for $Me_2As(S)OAs(S)Me_2$ **2**

Ab initio	PM3	Experimental	Type of vibration
218	208	201	As–O–As bend
279	269	264	As–O–As bend + sym. stretch
336	278	334	As–O–As bend + antisymmetric stretch
509	369	373	As–O–As sym. stretch + in-phase As = S stretch
541	427	482	Antisymmetric As = S stretch + symmetric As–O–As stretch
577	447	523	Symmetric As–O–As stretch + small contribution from As = S in-phase stretch
671/673	583/595	615	Symmetric As–C stretch
694/695	584/596	640	Antisymmetric As–C stretch
966	979	920	Antisymmetric As–O–As stretch

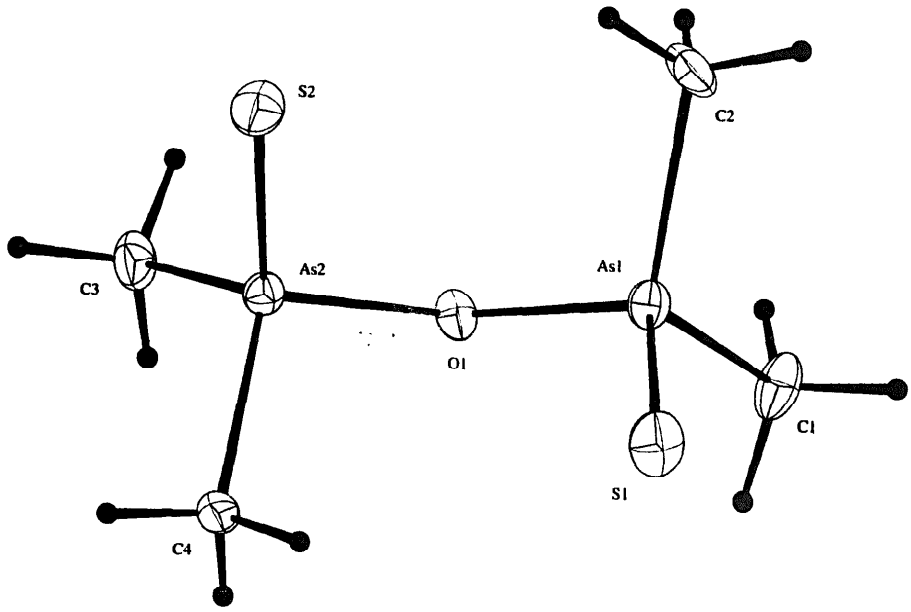

Fig. 3. Structure of $AsMe_2(S)OAs(S)Me_2$ **2** showing the atom numbering scheme.

localised on the As–S–As bridge (antisymmetric stretch), while in **2**, there are no pure As–O–As modes. The As = S and As = O vibrations are also well localised in **1** while the As = S stretches in **2** are mixed with the As–O–As bending mode. Overall agreement with experimental frequencies is better for the PM3 than for the present ab initio values. Better basis sets in the ab initio approach would probably reduce the differences, but even these crude estimates are helpful for giving an approximate description of the normal modes. The ab initio and PM3 calculated spectra were matched, using the facilities offered by the SPARTAN 4.0 graphics interface, by superposing the vibrating molecules on the screen. Further matching of the experimental spectra

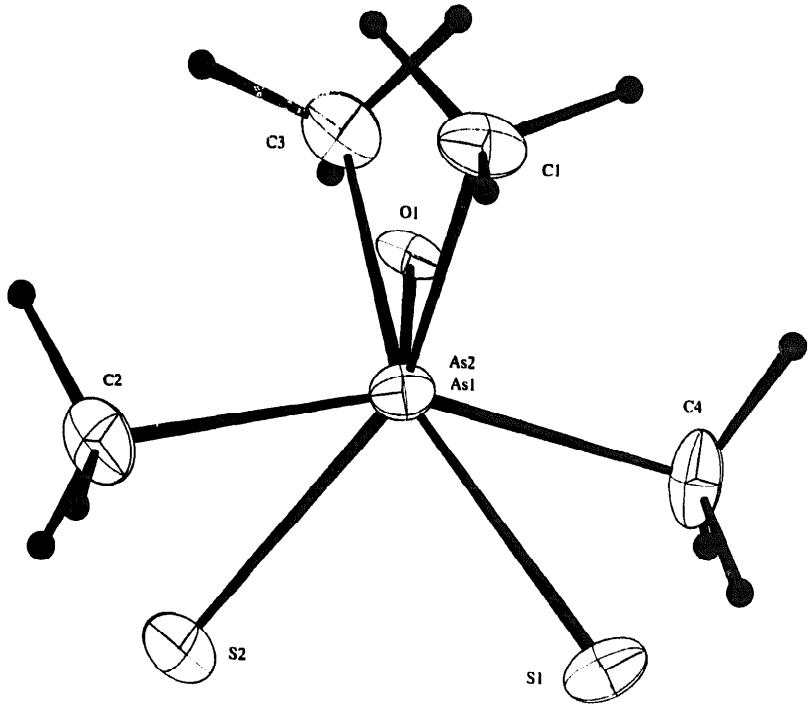

Fig. 4. Projection of the structure of **2** down the *As* ··· *As* vector.

Table 3
Important bond lengths (Å) and bond angles (°) from X-ray diffraction compared with ab initio 3-21G* values for $Me_2As(S)OAs(S)Me_2$ **2**

	X-ray	Ab initio 3-21G*
As(1)–S(1)	2.071(4)	2.054
As(1)–O(1)	1.786(9)	1.763
As(1)–C(1)	1.90(1)	1.927
As(1)–C(2)	1.93(1)	1.928
As(2)–S(2)	2.068(4)	2.054
As(2)–O(1)	1.785(8)	1.763
As(2)–C(3)	1.93(1)	1.927
As(2)–C(4)	1.92(1)	1.928
S(1)–As(1)–O(1)	112.5(3)	114.59
S(1)–As(1)–C(1)	115.6(5)	115.92
O(1)–As(1)–C(1)	97.9(5)	98.61
S(1)–As(1)–C(2)	116.9(5)	114.45
O(1)–As(1)–C(2)	104.0(5)	104.30
S(2)–As(2)–O(1)	114.0(3)	114.59
S(2)–As(2)–C(3)	116.8(5)	115.92
O(1)–As(2)–C(3)	97.3(5)	98.61
S(2)–As(2)–C(4)	115.2(5)	114.45
O(1)–As(2)–C(4)	104.1(5)	104.30
C(3)–As(2)–C(4)	107.3(7)	107.23
As(1)–O(1)–As(2)	125.0(5)	133.68
C(1)–As(1)–C(2)	107.7(7)	107.22

and calculated values considered the positions of the noncoupled As–C stretching modes and the well-known bands of methyl groups.

2.4. Structure of $AsMe_2(S)OAs(S)Me_2$

The X-ray diffraction study confirms that **2** is the oxygen-bridged isomer, $AsMe_2(S)OAs(S)Me_2$, and a diagram showing the molecular structure and the atom numbering scheme is given in Fig. 3. A view down the ***As*** · · · ***As*** vector is in Fig. 4. Important bond lengths and angles are listed in Table 3, which also includes values calculated by ab initio 3-21G* methods that show good agreement with the experimental values.

Although the molecule has no formal symmetry, the two halves are very similar, and the oxygen bridge is symmetrical. The As–O–As bridge angle, 125.0(5)°, is smaller than those in related As(III)–O–As(III) systems, e.g., $AsPh_2$–O–$AsPh_2$ (137°) [16] and 10,10-bis(phenoxarsine)oxide [17], and also smaller than that in the recently reported arsenic(V) addition compound, $Cl_3As = O \cdot AsF_5$ (129.1°) [18]. The smaller angle may be related to packing effects in the crystal, but a simple picture would suggest a smaller angle in As(V)–O–As(V) systems compared with As(III)–O–As(III) analogues as a consequence of weaker $(p \rightarrow d)\pi$ interactions. Flexibility of As–*O*–As angle is, however, supported by the value (133.6°) calculated for the gas phase structure by ab initio methods, and by the low value (208 cm^{-1}) calculated for the As–O–As bending mode.

The molecule has an overall gauche conformation with values for the S(1)-As(1)-O(1)-As(2) and As(1)-O(1)-As(2)-S(2) torsion angles of 45.9 and 41.7°, respectively; the S(1)-As(1)-As(2)-S(2) torsion angle is 79.0°. These are in reasonable agreement with values calculated for the gas phase structure of 54.47, 54.47 and 97.62°, respectively.

There is the expected distorted tetrahedral geometry about arsenic with angles ranging between ca. 97 and 117°. Arsenic–sulfur distances, 2.071(4) 1 and 2.068(4) Å, are comparable with As = S separations in $AsMe_2(S)SAsMe_2$ (2.075 Å) [14], $As(F\text{-}C_6H_4)_2(S)CH_2As(C_6H_4\text{-}F)$ (2.076 Å) [3] and $AsR_2(S)CH_2As(S)R_2$ (R = Et, 2.082 Å; R = *p*-tolyl, 2.073 Å) [3] but shorter than those in $AsEt_3(S)$ (2.114 Å [19]), $AsPh_3(S)$ (2.090 Å [20]) and $AsPh_2Et(S)$ (2.081 Å [21]). From an electron diffraction determination, the As = S distance in $AsMe_3(S)$ is 2.059 Å [22].

3. Experimental

Tetramethyldiarsine disulfide was prepared according to literature data by treating $AsMe_2(O)OH$ with H_2S in ethanolic solution [23] or by adding HCl to an ethanolic solution of sodium dimethyldithioarsinate.

3.1. Reaction of $AsMe_2(S)SAsMe_2$ with t-BuOOH

The reaction was carried out under anhydrous conditions in an argon atmosphere with previously dried solvents. The solution obtained by dissolving $AsMe_2(S)SAsMe_2$ (2.1 g, 7.6 mmole) in anhydrous benzene (20 ml) was stirred with *t*-BuOOH (2.55 ml of 3 M in isooctane) at room temperature. Fractional crystallisation in the atmosphere of the resulting solution first gave white crystals of **2** (melting point 163°C, 27% yield), while crystals of **1** (melting point 128°C, 48% yield), as the monohydrate from reaction with adventitious moisture, were isolated on further concentration of the mother liquor. Both solids were then recrystallised to constant melting point. Anal. Found: C, 15.8; H, 4.9. $C_4H_{14}O_2S_2As_2$ (**1** · H_2O) Calc.: C, 15.6; H, 4.5%. Found: C, 16.6; H, 4.4. $C_4H_{12}OS_2As_2$ (**2**) Calc.: C, 16.6; H, 4.4%.

3.2. Calculations

All calculations were carried out with the Spartan 4.0 package of programs [24], installed on an Indy machine. Full semiempirical PM3 [25] optimisations (gradient norm = 0.0001) were performed on the conformers of **1** and **2** generated by rotations of 30° around the As–E (bridge) bonds. For the lowest energy conformers, frequency calculations were also completed. A search for a possible transition state for the rearrangement of **1** to **2**

used the linear synchronous transit (LST) method [26], followed by optimization with the TS keyword of Spartan. Once the TS point was localised, optimisations (and frequency calculations) were repeated by the RHF/3-21G* ab initio method.

3.3. Crystal structure of $AsMe_2(S)OAs(S)Me_2$

3.3.1. Crystal data

$C_4H_{12}As_2OS_2$, $M = 290.1$, monoclinic, space group $C2/c$, $a = 27.47(1)$, $b = 6.280(3)$, $c = 12.087(4)$ Å, $\beta = 96.89(4)°$, $U = 2070.0$ Å^3, $Z = 8$, Dc = 1.86 g cm^{-3}, $F(000) = 1136$, $\mu = 67.7$ cm^{-1}, Mo–Kα radiation, $\lambda = 0.710\ 73$ Å, crystal size = 0.5 × 0.3 × 0.3 mm^3.

3.3.2. Structure determination

A suitable crystal was mounted on a glass fibre, and diffraction data were collected at 150 K using a Delft Instruments FAST TV area detector diffractometer, situated at the window of a rotating anode generator operating at 50 kV and 45 mA. Data were collected for 4276 reflections of which 1580 were unique (merging $R = 0.080$) and 881 reflections with $I > 4\sigma(I)$ were considered observed and corrected for Lorentz and polarisation effects and for absorption (DIFABS) [27].

The structure was solved by direct methods using SIR92 [28] and refined by full matrix least squares methods on F using the CRYSTALS [29] programs and scattering factors for neutral atoms. After refinement of the heavy atom positions with anisotropic thermal parameters, the methyl group hydrogens were placed at their calculated positions [d(C–H) = 1.0 Å] and refined riding on their perspective carbon atoms [U_{iso} (H) = 1.3 × U_{equ} (C)]. Final convergence (83 least squares parameters, maximum shift: esd = 0.01) occurred at $R = 0.041$ ($R_w = 0.052$); max. and min. residual electron densities were 0.73 e Å^{-3} and −0.64 e Å^{-3}, respectively. Final values for the atomic coordinates are collected in Table 4, while tables of the hydrogen atom coordinates and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

Table 4
Atomic coordinates and equivalent isotropic displacement coefficients (Å^2) for (2)

Atom	x	y	z	U_{eq}
As(1)	0.57515(5)	0.1881(2)	0.5021(1)	0.0219
As(2)	0.67460(5)	0.3724(2)	0.6252(1)	0.0199
S(1)	0.5445(1)	0.1602(7)	0.6498(3)	0.0302
S(2)	0.6993(1)	0.0737(6)	0.6775(3)	0.0300
O(1)	0.6259(3)	0.368(1)	0.5132(6)	0.0189
C(1)	0.5355(5)	0.327(3)	0.384(1)	0.0287
C(2)	0.6006(6)	−0.068(2)	0.443(1)	0.0298
C(3)	0.7194(5)	0.548(2)	0.553(1)	0.0287
C(4)	0.6496(5)	0.544(3)	0.737(1)	0.0268

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