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Aspects of the chemistry of vinylarsenic compounds. The preparation of divinylarsinic acid, tetravinyldiarsine oxide, and tetravinyldiarsine, and the X-ray crystal structure of the helical divinylarsinic acid

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Abstract

Tetravinyldiarsine (1) was prepared by coupling divinylarsenic(III) bromide (6) with lithium dispersion in diethyl ether. Tetravinyldiarsine oxide (2) and divinylarsinic acid (3) were obtained as primary and secondary by-products, respectively. Compound 3 crystallizes in the monoclinic space group $P2_1/n$, with $a = 7.714(6)$ Å, $b = 7.293(8)$ Å, $c = 10.799(8)$ Å, $\beta = 92.27(3)°$, $\rho_c = 1.77$ g cm^{-3} for $Z = 4$. Least squares refinement, based on 429 observed reflections, led to a final R of 0.057. The molecules are linked by hydrogen bonds to form an extended, linear, helical chain along the twofold screw axis. The O $\cdots$ H–O distance is 2.53(1) Å, indicative of strong hydrogen bonding. The As–O bond distances are significantly different with As–O(1) = 1.721(6) Å and As=O(2) = 1.617(6) Å. The As–O(1) $\cdots$ O'(2) and As=O(2) $\cdots$ O'(1) intermolecular bond angles are 111.5(4)° and 128.7(4)°, respectively. Dihedral angles between planes containing the vinyl carbons and the As=O bond are −5.2° and 12.2°, which strongly suggests the presence of conjugative interaction. Spectroscopic data are reported for compounds 1 and 2. Compound 3 was characterized by melting point and ^{1}H and ^{13}C NMR, IR and UV spectroscopic techniques.

1. Introduction

Among the compound semiconductors, GaAs is perhaps one of the most widely studied. Its direct bandgap makes it a good candidate for laser applications, while a range of (Al,Ga)As compositions find use in an array of high-speed electronic devices. One popular method for the production of epitaxial thin films of GaAs is organometallic vapor phase epitaxy (OMVPE) [1]. In the common manifestation of the OMVPE synthesis, AsH_3 is the primary source of the Group 15 element for the final material. The combination of the high vapor pressure and high toxicity of this congener of ammonia has led researchers to explore a variety of alternate routes to produce high quality GaAs. Significant success in this area has been achieved by the total replacement of As–H bonds in the "single-source" precursors of the general form $[R_2MER'_2]_n$ (M = Al,

Ga, In; E = P, As, Sb, Bi; R = Me, Et; R' = ^{i}Pr, ^{t}Bu; n = 2, 3) [2]. The most successful alternative to date, however, is ^{t}BuAsH$_2$. This primary arsine, a liquid at ambient conditions, is both easier to contain and less toxic than gaseous AsH_3. Most importantly, carbon incorporation into thin films of GaAs grown by OMVPE from this precursor is minimal when compared with results from other alkyl arsines [3]. Another potential source of elemental arsenic, the tetraalkyldiarsines, is indicated both in results from 70 years ago [4], and in a recently published study [5] (eqn. (1)). Accordingly, we recently initiated an investigation into the feasibility of utilizing this class of compounds as relatively less toxic precursors to the arsenic necessary for GaAs growth.

$$3R_2As\text{–}AsR_2 \rightleftharpoons 4AsR_3 + 2As \tag{1}$$
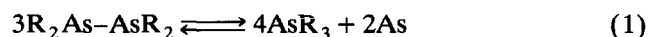
The simplest tetraalkyldiarsine, $(H_3C)_2As\text{–}As(CH_3)_2$, given the trivial name of cacodyl, was discovered in 1760 by Cadet. It is claimed as the first report of a compound containing a metal–carbon bond [6]. Cacodyl oxide also was produced in the same reaction and characterized by Bunsen at a later date. Although

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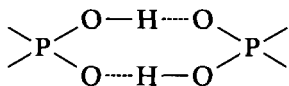[1] Permanent address: Department of Chemistry, Spring Hill College, Mobile, AL 36608, USA.

Fig. 1. Dimeric structure found in di(t-butyl)phosphinic acid and all three previously reported arsinic acids, other than the diphenyl derivative.

a fair amount of research has been conducted over the ensuing years on cacodyl and other diarsines, scant attention has been paid to molecules having unsaturated hydrocarbon substituents, with the exception of phenyl derivatives [7]. The prevailing wisdom in OMVPE has been that the presence of any sp^2 or sp carbon in the precursors will lead to incorporation of carbon in the final thin film [1]. Such incorporation is not only disadvantageous, it often totally destroys the desired electronic properties of the film. Conversely, there are reports which indicate that this notion may not always be correct [8]. Specifically, in the instance where one desires to impart photosensitivity to a class of molecules, the inclusion of π-bonding substituents may be of great advantage. As a result of these requirements, we set about the synthesis of tetravinyl-diarsine. Along the route, we characterized tetravinyl-diarsine oxide and divinylarsinic acid. Several noteworthy features were observed in the solid state structure of the acid, as determined by single crystal X-ray diffraction. We now report on these results and related studies of vinylarsenic compounds.

X-Ray crystal structure analyses have been published for a variety of carboxylic [9] and phosphinic [10–20] acids but, to date, the structures of only three arsinic acids [21–23] have been determined fully. Two general structural types are known for these classes of

molecules, both of which are characterized by intermolecular hydrogen bonding. In the first type, pairs of molecules form a dimer containing two hydrogen bonds which, in turn, are part of an eight membered ring (Fig. 1). In the second type, each molecule forms hydrogen bonds to two different neighboring molecules. As a result, an extended, linear chain of atoms is formed.

Carboxylic acids generally form dimers, with the notable exception of those acids where the alkyl group is small [9]. For example, both formic and acetic acids exist in the solid state as planar chains. On the other hand, most phosphinic acids have a helical chain structure, perhaps, at least in part, due to the larger size of the phosphorus atom when compared with carbon. Sterically hindered di(t-butyl)phosphinic acid [18,19] and di(t-pentyl)phosphinic acid [20], however, crystallize in the dimeric structure.

It is surprising then that an X-ray diffraction crystal structure analysis of dimethylarsinic acid [21] has shown that it exists as a dimer. Di(n-butyl)arsinic acid (4) [22] also forms a dimer, and cell constant data [24] strongly suggest that at least the diethyl, di(n-propyl) and C_5 to C_8 analogs also exist as dimers in the solid state. In fact, it is likely that all straight chain saturated hydrocarbon arsinic acids, C_1 to C_{20}, form dimers, although a phase transition, thought to be due to reorientation of the alkyl chains and corresponding changes in intrachain van der Waals contacts, has been observed just prior to the melting point for C_6 and longer side chain acids [25]. In contrast, diphenylarsinic acid (5) has been determined to uniquely adopt the helical chain structure [23]. In this paper, we report the crystal structure of divinylarsinic acid (3). The steric and electronic properties of the vinyl group make this molecule a
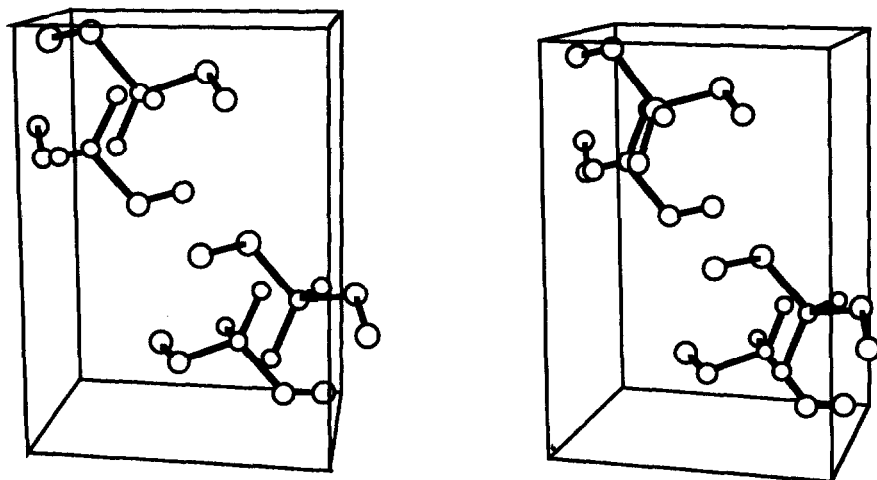

Fig. 2. Stereoscopic projection of the unit cell and heavy atom contents for divinyl arsinic acid (3).

good candidate for comparison of its solid state structure with the known structures of the rather limited class of other arsinic acids.

2. Results and discussion

Molecules of **3** form a linear helix in the solid state, bound together by hydrogen bonds between each molecule and two neighboring molecules. A representation of the crystallographic unit cell is depicted in Fig. 2. Relevant crystal and data collection parameters are given in Table 1. Positional parameters are supplied in Table 2 and selected interatomic distances and angles are given in Table 3. The atoms bound to arsenic form a slightly distorted tetrahedron. The average C-As-O(1) angle, 104.6(6)°, is somewhat less than the ideal tetrahedral angle, while the average C-As=O(2) angle, 112.3(6)°, is slightly greater (ortep representation given in Fig. 3). Similar bond angles are observed in **5**, where the corresponding average angles are 104.0(1)° and 111.7(1)°, respectively. The C-As-C and O-As-O angles are, within experimental error, as expected from the atomic geometry (Table 3). A somewhat larger O-As-O angle, 114.8(1)°, was found in the more sterically demanding **5**.

TABLE 1. Crystal and refinement data for divinylarsinic acid (**3**)

Formula	$AsC_4H_7O_2$
Molecular weight	162.02
Color of crystal	Colorless
Crystal size (mm³)	0.30 × 0.30 × 0.30
Diffractometer	CAD-4
Radiation	Mo Kα
Scan speed (° min⁻¹)	1.0
Abs. coeff. (cm⁻¹)	54.8
Scan technique	θ-2θ
2θ scan range (°)	2-50
Scan width (°)	1.8
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	7.714(6)
b (Å)	7.293(8)
c (Å)	10.799(8)
β (deg)	92.27(3)
V (Å³)	607.1
Z	4
ρ (calcd.) (g cm⁻³)	1.77
ρ (found) (g cm⁻³)	1.75
Data collected	560
Unique data with $I \geq 3\sigma$ (I)	429
Weighing factor	$1/\sigma$ (F^2)
Standard reflections	3
LS parameters	82
R (F)	0.057
R_w (F)	0.065

TABLE 2. Atomic coordinate for divinylarsinic acid (**3**)

Atom	x	y	z
As	0.1252(2)	0.3269(2)	0.6568(1)
C1	−0.073(2)	0.187(2)	0.6195(14)
C2	0.287(2)	0.314(2)	0.5269(12)
C3	−0.123(2)	0.055(2)	0.6915(13)
C4	0.434(2)	0.239(2)	0.5441(14)
O1	0.050(1)	0.549(1)	0.6544(8)
O2	0.209(1)	0.274(1)	0.7917(8)
H1	−0.2245(0)	−0.0133(0)	0.6699(0)
H2	−0.0580(0)	0.0282(0)	0.7658(0)
H3	−0.1399(0)	0.2121(0)	0.5455(0)
H4	0.5122(0)	0.2334(0)	0.4785(0)
H5	0.4656(0)	0.1872(0)	0.6226(0)
H6	0.2566(0)	0.2647(0)	0.4481(0)

TABLE 3. Selected interatomic distances and angles in divinylarsinic acid (**3**)

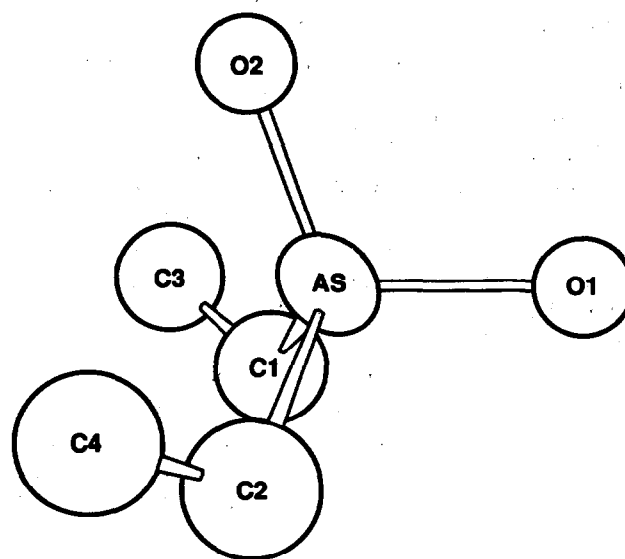| Atoms	Distance (Å)	Atoms	Angle (°)
As-C(1)	1.87(1)	C(1)-As-C(2)	111.5(5)
As-C(2)	1.92(1)	C(1)-As-O(1)	104.0(4)
As-O(1)	1.721(6)	C(1)-As-O(2)	111.0(4)
As-O(2)	1.617(6)	C(2)-As-O(1)	105.3(4)
C(1)-C(3)	1.30(2)	C(2)-As-O(2)	113.5(4)
C(2)-C(4)	1.26(2)	O(1)-As-O(2)	111.0(3)
O(1)-O(2')	2.53(1)	As-C(1)-C(3)	122.0(9)
		As-C(2)-C(4)	121.3(9)
		As-O(1)-O(2')	111.5(4)
		As-O(2)-O(1')	128.7(4)

Fig. 3. An ortep representation of the solid state structure of divinyl arsinic acid (**3**), with thermal ellipsoids drawn at the 70% probability level, and hydrogen atoms omitted for clarity.

The average As–C bond distance observed for **3**, 1.90(1) Å, is within experimental error of the range of values found in other arsinic acids, 1.89–1.92(2) Å [21–23]. The As–O bond distances [26*], As–O(1) = 1.721(6) Å and As–O(2) = 1.617(6) Å, are significantly different, indicating an asymmetric position for the proton involved in hydrogen bonding. The longer As–O bond distance is not significantly different from related distances in **4** and **5**; however, the shorter As–O distance, although only slightly decreased from the analogous bond length in **5** (1.639(2) Å) is significantly shorter than the related bond length found in the dimeric **4** (1.67(1) Å).

Additional insight into the differences present between **3** and **4** comes from comparison of their IR data. For **4**, only one arsenic-oxygen stretching vibration was reported in the infrared spectrum, at 890 cm^{-1} [27]. These workers interpreted this to be the value expected for an average bond order of 1.5. For **3**, in addition to the likely vinyl C–H stretches at 980 and 970 cm^{-1}, we observe strong IR absorptions at 880, 847, and 750 cm^{-1}. The 750 cm^{-1} band corresponds well with the 776 cm^{-1} calculated for a "pure" As–O single bond [28*]. The 880 cm^{-1} absorption could be either As=O or C=C; however, the 847 cm^{-1} vibration is most likely As=O. Frequencies of 837 and 878 cm^{-1} are recorded for AsO^{-3} [29].

The distance between the hydrogen-bonded oxygen atoms in **3** (2.53(1) Å) indicates strong hydrogen bonding. This distance and the As–O–O angles, with As–O(1) ··· O′(2) = 111.5(4)° and As=O(2) ··· O′(1) = 128.7(4)°, are related closely to the analogous values found in **5** (2.52(2) Å, 112.7(1)° and 120.6(1)°) [30*]. A residual electron density of approximately 0.5 e Å^{-3}, labeled H(7), was located in an asymmetric and off-line position between the hydrogen-bonded oxygen atoms in **3**, with O(1)–H(7) = 0.91 Å, O(2)–H(7) = 1.81 Å and O(1)–H(7) ··· O′(2) = 133°.

The second most important intermolecular interaction within the helical chains may be the dipole–dipole attraction present between the relatively electropositive As and O′(2) in one of the two neighboring molecules. The relevant As ··· O′(2) distance is 3.540(6) Å, just larger than the sum of the van der Waals radii (3.4 Å).

An interesting feature of this structure follows from the dihedral angles (Table 4) formed between the vinyl planes defined by two doubly bonded carbon atoms and the arsenic atom, and the plane defined by O(2), As and one of the C atoms bonded to As. The values
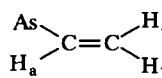
are 12.2° and −5.2°. The fact that both angles are close to zero strongly suggests that conjugation exists between the C=C and As=O multiple bonds. This is in contrast to the corresponding angles in **5**, which we calculate (using the positional parameters found in the original paper) to be 29.0° and −16.5°. A comparison of conjugation in known phosphinic and arsinic acid structures is worthwhile. It has been reported that the influence of phenyl groups on the acid dissociation constant of diphenylphosphinic acid is not additive [31], and it was suggested that this was due to steric interaction between the rings which limits conjugation. On the other hand, the effect of vinyl groups in divinylphosphinic acid was found to be additive. Finally, in **3**, both vinyl planes are rotated about their As–C bonds in order to bring the hydrogen atoms bound to C(1) and C(2) slightly closer to O(1) and away from one another. This effect is greatest for the vinyl group on the same side of the arsenic atom as the hydrogen bond.

The mass spectra of **1** and **2** each contain a base peak corresponding to AsC$_2$H$_2$. Both give parent ions; **1** at 258 and **2** at 274 m/e. The second highest mass fragment observed in each spectrum is assigned to the parent ion with loss of three vinyl groups (**1**, 177; **2**, 193). The most interesting feature present in the data for **1** is the observation of a fairly intense signal (approximately 20% of the base peak) at $m/e = 150$, corresponding to As$_2$. All compounds gave unexceptional ABX type ^{1}H NMR spectra (Table 5) which were well resolved with the exception of **3**, where some minor second order effects were observed.

TABLE 4. Selected dihedral angles for divinylarsinic acid (3)

Atom 1	Atom 2	Atom 3	Atom 4	Angle (°)
C(4)	C(2)	As	O(2)	12.2
C(3)	C(1)	As	O(2)	−5.2
C(4)	C(2)	As	O(1)	133.8
C(3)	C(1)	As	O(1)	−124.6

TABLE 5. 300 MHz ^{1}H NMR data [a] for

$$\begin{array}{c} As \diagdown \\ \diagup C=C \diagdown \\ H_a \quad\quad H_b \end{array} \begin{array}{c} H_c \\ \diagup \end{array}$$

Compound	H$_a$	H$_b$	H$_c$	$J_{a,b}$	$J_{a,c}$	$J_{b,c}$
1	6.58	5.92	5.66	11.4	18.6	1.4
2	6.75	5.96	5.77	11.4	18.6	1.6
3 [b]	6.51	6.35	6.25	11.4	18.6	~0
6	6.95	6.00	5.89	11.1	18.6	~0

[a] Chemical shifts in ppm and coupling constants in Hz, in CDCl$_3$ unless indicated otherwise. [b] In D$_2$O.

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

3. Summary

The reaction of divinylarsenic(III) bromide (6) with lithium dispersion in diethyl ether produces tetravinyldiarsine (1), tetravinyldiarsine oxide (2) and divinylarsinic acid (3). Compound 3 crystallizes in a helical chain comparable to that observed for the diphenylarsinic acid analog (5). There is evidence for a conjugative interaction of the two vinyl groups with the As=O in compound 3; such interactions appear to be limited for 5. Additional explorations of the organometallic chemistry ·of 1 and its potential for utilization in materials science are planned and will be reported in the future.

4. Experimental details

4.1. General comments

^{1}H and ^{13}C NMR spectra were obtained at 300 and 75.54 MHz, respectively, on a Varian Gemini 300 spectrometer. Compounds 1 and 2 were dissolved in $CDCl_3$ and referenced to the residual ^{1}H and ^{13}C resonances at 7.24 and 77.0 ppm, respectively. Compound 3 is sparingly soluble in D_2O, which was used to reference the ^{1}H spectrum at 4.63 ppm. A small amount of methanol was added to the D_2O to serve as a reference for the ^{13}C spectrum at 49.3 ppm. Mass spectra were obtained using a Hewlett Packard Series II 5890 gas chromatograph equipped with a model 5971 mass selective detector containing an electron impact source operating at 70 eV. Infrared data were collected on a Perkin-Elmer 983 spectrometer using powdered 3 spread on KBr plates. The UV spectrum for 3 was obtained down to 200 nm on a Cary 14 spectrometer upgraded with an OLIS controle module, with D_2O as the solvent. The melting point for 3 was obtained in a sealed capillary under nitrogen and is uncorrected. Diethyl ether and pentane were dried and distilled under nitrogen over lithium aluminum hydride. Chloroform-d_3 was stored over freshly activated molecular sieves. Vacuum Atmospheres inert atmosphere glove boxes were employed with an atmosphere of $N_{2(g)}$ purified by a model HE Dri Train.

4.2. Preparation of 1, 2, and 3

Divinylarsinic acid (3) was prepared incidentally as a by-product during the synthesis of tetravinyldiarsine (1). An oven dried flask was charged with 160 mg (6.9 mmol, 40% excess) of 30% lithium dispersion. After washing with diethyl ether to remove the mineral oil, 4 ml of diethyl ether was added, the mixture was brought to reflux and 1.04 g (5.0 mmol) of divinylarsenic(III) bromide (6) [32,33] was added over a period of 1 h under nitrogen. Reflux was continued for an additional

24 h. The product mixture, consisting of 1:2:6 in a ratio of 7:2:1 by ^{1}H NMR, then was evaporated to dryness and pentane was added. Filtration was carried out under nitrogen, and the mixture was stored under a rubber septum wrapped with Parafilm but no other precautions were taken to exclude oxygen or moisture. Two weeks later, crystals were observed growing from the bottom of the flask. Over time, both cube-shaped and needle-like crystals of 3, each with the same lattice parameters, were produced, having a melting point of 91–92°C. The crystals were separated by anaerobic filtration. The filtrate consisted predominately of 2 as identified by 1H NMR spectroscopy. Subsequently, pure 1 has been prepared by this route without the incidental formation of 2 and 3.

4.2.1. Preparation of 1

Tetravinyldiarsine (1) was prepared by a slight modification of the route given above. The reaction flask was rinsed with trimethylchlorosilane, oven dried and charged with 950 mg (34.2 mmol, 10% excess) of 25% lithium dispersion in a nitrogen filled glovebox. The flask was equipped with a water cooled reflux condenser and a rubber septum, removed from the glovebox, and the dispersion was washed free of mineral oil with several portions of diethyl ether. Diethyl ether (10 ml) was added, followed by 6.5 g (31.1 mmol) of 6 dissolved in diethyl ether, over a period of 40 min. The rate of addition sufficed to keep the reaction at reflux without external heating. Following addition, the reaction flask was placed in a 40°C oil bath. After 2 h, 5 ml of diethyl ether was added, at which point it was noticed that a small amount of reflective powder, probably elemental arsenic, was present. Reflux was continued for another 3 h. The reaction mixture then was evaporated to dryness, treated with pentane and filtered under nitrogen. Following removal of the pentane, 1 distilled at ambient temperature and 0.2 mmHg as a colorless liquid.

4.3. Spectroscopic data

^{1}H NMR data are given in Table 5 for compounds 1–3 and 6 [34*].

^{13}C NMR: Compound 1 ($CDCl_3$): 128.3 (^1J(CH) = 158.7, t); 136.7 (^1J(CH) = 161.1, d). Compound 3 (D_2O, methanol internal reference): 129.1, 137.5 (lack of solubility inhibits assignment of peaks).

IR: Compound 1 (neat): 3140vs, 3040m, 2970s, 2920m, 2220vw, 1940vw, 1850br,w, 1570m, 1370s, 1250m, 1230m, 995sh, m, 970s, 925s, 800vw, 735w, 585m, 525s. Compound 3 (neat): 1400m, 1380m, 1245m, 1010m, 980m, 970s, 880s, 847m, 750s, 615m, 580m.

UV/vis: Compound 1 (hexane): end absorption with a peak at 281 nm, ϵ = 8500. Compound 3 (D_2O): end absorption tailing to approximately 260 nm.

MS: Compound **1**: 258 (15% base, M^+), 177 ($As_2C_2H_3$), 151 (As_2H), 150 (As_2), 129 (AsC_4H_6), 128 (AsC_4H_5), 127 (AsC_4H_4), 101 (base, AsC_2H_2). Compound **2**: 274 (8% base, M^+) 193 ($As_2OC_2H_3$), 177 ($As_2C_2H_3$), 167 (As_2OH), 151 (As_2H), 129 (AsC_4H_6), 127 (AsC_4H_4), 101 (base, AsC_2H_2).

4.4. Crystallography of 3

A colorless, cube shaped crystal measuring approximately $0.3 \times 0.3 \times 0.3$ mm^3 was placed in a glass capillary inside an inert atmosphere glove box. The intensity data were measured on a CAD4 Enraf-Nonius diffractometer (Mo $K\alpha$ radiation, monochromated, θ-2θ scans). No absorption correction was done ($\mu = 54.8$) in view of the uniformity and size of the crystal. A total of 560 reflections were measured for $2\theta \leq 50$, of which 429 were considered to be observed [$I \geq 3\sigma(I)$]. The structure was solved by Patterson and difference Fourier techniques and refined by full-matrix least squares methods [35*]. In the final refinement, anisotropic thermal parameters were used for non-hydrogen atoms. Hydrogen atom parameters were calculated assuming idealized carbon atoms geometries. Hydrogen atom contributions were included in the structure calculations, but their parameters were not refined. The final discrepancy indices were $R = 0.057$ and $R_w = 0.065$. The final difference Fourier map was essentially featureless with the largest peak, 0.7 e Å^{-3}, near the As atom.

5. Supplementary material

A listing of atomic anisotropic thermal parameters (1 page) and observed and calculated structure factors (2 pages) is available from the authors.

Acknowledgments

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26 See ref. 23 for an extended comparison of As=O and As=OH bond lengths in structures of organoarsenic acids.

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34 Attempts to secure a satisfactory elemental analysis for **1** proved difficult. Samples sealed in ampoules in an inert atmosphere box were submitted for analysis and the results were observed to be dependent upon the length of time elapsed from unsealing to analysis. Found (1 day lapsed time): C, 34.88; H, 4.25. Found (3 days lapsed time): C, 31.38; H, 4.30. $C_8H_{12}As_2$ calcd.: C, 37.24; H, 4.69%.

35 All computations were performed on a PDP11/34 computer with the aid of the Structure Determination Package crystallographic program library obtained with the purchase of the X-ray equipment.