Journal of Organometallic Chemistry 745-746 (2013) 80–85

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

A re-investigation of arsenoacetic acid, $(AsCH_2COOH)_n$

Brian K. Nicholson [a,*], Peter S. Wilson [a,b], Adelle Nancekivell [a]

[a] Chemistry Department, University of Waikato, Private Bag 3105, Hamilton 3240, New Zealand
[b] Institute for Applied Ecology New Zealand, School of Applied Sciences, Auckland University of Technology, Private Bag 92006, Auckland 1142, New Zealand

ARTICLE INFO

Article history:
Received 23 May 2013
Received in revised form
10 July 2013
Accepted 18 July 2013

Keywords:
Arsenic
Cyclopolyarsine
X-ray crystal structure
Electrospray ionisation mass spectrometry

ABSTRACT

Detailed spectroscopic data have been obtained for arsonoacetic acid, $As(CH_2COOH)O_3H_2$, and its barium and sodium salts. The X-ray crystal structure of the free acid is isomorphous with phosphonoacetic acid. Reduction gave the As(I) compound arsenoacetic acid, $(AsCH_2COOH)_n$ which was shown by ESI-MS to contain cyclic species based on As–As bonds, with n mainly 3–6. The X-ray crystal structure of the hexamer was determined as the pyridine solvate and shown to have a hexacyclic As_6 ring in a puckered chair conformation, with $-CH_2COOH$ groups in equatorial sites, each H-bonded to a pyridine molecule in the lattice.

1. Introduction

Interest in the chemistry of organo-arsenic(I) chemistry can be traced to the historically important drug Salvarsan (also known as Arsphenamine) which Ehrlich introduced as a cure for syphilis in 1910 [1]. This compound, produced by reduction of 3-amino-4-hydroxyarsonic acid, was originally assigned the structure **1a** based on analogies with aryl–azo compounds. As=As double bonds, however, are only isolable with extremely bulky substituents [2], therefore polymeric or cyclic structures were subsequently proposed [3]. In support of the cyclic forms, recent ESI-MS studies on Salvarsan have shown that it consists of $(RAs)_n$ rings **2**, $n = 3–8$, with $n = 5$ and 6 being the most abundant [4]. For other derivatives, structural studies have now defined cyclic species $(RAs)_n$ for $n = 4$, 5, and 6 which all show puckered rings with As–As distances of *ca* 2.46 Å and As–As–As angles of around 90° [5].

A compound of this type that is still unresolved is arsenoacetic acid, the product of reduction of arsonoacetic acid **3**. This was first reported in 1923 by Palmer [6] and was assigned the structure **1b**. Even now it is represented as such in the Merck Index [7] where it is noted that it has had veterinary use as a tonic for horses. It has been patented as a fire retardant [8a] and as a treatment for premenstrual syndrome in women [8b] and has been used for treating chronic fatigue syndrome in horses [8c]. The original structure **1b** is clearly unlikely but there have been no modern studies concerning its chemistry, so we herein report the results of a re-investigation using modern techniques.

2. Experimental

ESI-MS was carried out on a Bruker MicrOTOF instrument, operating under standard conditions in negative ion mode, with samples made up in H_2O or 1:1 CH_3CN:H_2O (with the addition of pyridine), immediately before infusion. Peaks are reported as the m/z with the greatest intensity in the isotopic envelope. NMR spectra were recorded on a Bruker Avance 400 machine in D_2O or pyridine-d_5, and IR spectra were from a Perkin–Elmer Spectrum 100 run as KBr disks. Arsenoacetic acid was handled under an atmosphere of nitrogen using standard Schlenk techniques.

2.1. Synthesis of barium arsonoacetate, $Ba_3[As(CH_2COO)O_3]_2$

The barium salt of arsonoacetic acid was prepared using the Meyer reaction [9], as adapted by Palmer [6]. Arsenic trioxide (10 g, 51 mmol) was added to a hot aqueous solution of NaOH (10 g, 0.4 mol in 30 mL H_2O) and cooled to room temperature. Chloroacetic acid (4.8 g, 51 mmol) was added and stirred for 1 h. The clear solution was acidified with glacial acetic acid (16 mL) and, after cooling to 40 °C, the precipitated excess arsenic trioxide was filtered by suction and washed with water. The filtrate was poured into a hot solution of $BaCl_2 \cdot 2H_2O$ (18.5 g, 76 mmol) in H_2O (60 mL) and stirred for 5 min. Barium arsonoacetate was filtered by suction after the solution was allowed to stand overnight, and washed thoroughly with water. Yield 30 g, 75%. IR: (cm^{-1}) 3403(vs, br)

* Corresponding author. Fax: +64 7 838 4219.
E-mail address: b.nicholson@waikato.ac.nz (B.K. Nicholson).

0022-328X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jorganchem.2013.07.056

2994(w) 2946(w) 2430(m) 1582(vs) 1421(s) 1390(s) 1328 (w) 1269(m) 1176(m) 1100(m) 942(m) 882(vs, br) 774(w) 708(s) 685(m) 626 (m) 556(w) 466(m) 419(m).

2.2. Synthesis of sodium arsonoacetate $Na_3[As(CH_2COO)O_3]\cdot H_2O$

Barium arsonoacetate (22 g, 28 mmol) was added to a hot solution of anhydrous Na_2SO_4 (10.7 g, 75 mmol) in H_2O (50 mL) and stirred for 1 h at room temperature. Barium sulphate was filtered and the filtrate concentrated using a rotary evaporator. The product crystallised as the monohydrate (12.95 g, 85%) [6]. ^{1}H NMR: [D_2O] δ 3.16 (s, CH_2) ppm; $^{13}C\{^1H\}$ NMR: [D_2O] δ 42.6 (s, CH_2), 172.6 (s, COO^-) ppm. IR (cm^{-1}) 3321(vs) 3245(s) 2934(w) 2742(m) 2399(m) 1712(m) 1601(vs) 1408(vs) 1376(vs) 1335 (w) 1255(m) 1191(m) 1118(s) 935(s) 891(vs) 834(s) 793(w) 735(s) 699(m) 620(s) 542(m) 434(m) 405(w).

2.3. Synthesis of arsonoacetic acid $As(CH_2COOH)O_3H_2$

As described by Palmer [6], barium arsonoacetate (5.4 g, 7 mmol) was stirred in H_2SO_4 solution (1.2 mL conc. H_2SO_4, 24 mL H_2O) for 5 h and precipitated barium sulphate was filtered by suction. Solvent was removed *in vacuo* over conc. H_2SO_4 until crystallisation commenced. The free acid was extracted into absolute ethanol (6 mL) and remaining inorganic material filtered. Petroleum spirits (6 mL) was added to the filtrate, which was dried over concentrated H_2SO_4 *in vacuo* until crystallisation commenced. Although a little unusual, the method was followed as described. The final product was washed with petroleum spirits (1.54 g, 60%).

Higher yields of better purity were obtained following a method described by Rozovskaya et al. [10] and Sparkes and Dixon [11]. Barium arsonoacetate (1.3 g, 5.04 mmol) was stirred for 30 min with a sulfonated polystyrene resin (AmberliteR IR-120, 10 mL wet volume) in its H^+ form. The solution was filtered and water removed using a rotary evaporator leaving a white powder, pure arsonoacetic acid (0.50 g, 80%). Found: C, 13.27; H, 2.78%; $As(CH_2COOH)O_3H_2$ requires: C, 13.06; H, 2.74%. ^{1}H NMR: [D_2O] δ 3.73 (s, CH_2) ppm. $^{13}C\{^1H\}$ NMR: [D_2O] δ 39.3 (s, CH_2), 168.0 (s, COO^-) ppm. IR: (cm^{-1}) 3500–2600(vs, br) 2999(w) 2936(w) 2404(m) 1882 (m) 1688(vs) 1449(w) 1389(w) 1306(m) 1239 (w) 1215 (w) 1139(m) 1115(w) 993(m) 891(vs, br) 853(m) 795(s) 776(s) 662(m) 423(s). ESI-MS: [H_2O] m/z 550.804 (15%) calc for $[3M - H]^-$ 550.798; 532.793 (16%) calc for $[3M - H_2O - H]^-$ 532.787; 366.867 (52%) calc for $[2M - H]^-$ 366.863; 348.856 (29%) calc for $[2M - H_2O - H]^-$ 348.852; 260.875 (9%) calc for $[C_2As_2H_7O_5]^-$ 260.873; 182.929 (100%) calc for $[M - H]^-$ 182.927; 138.940 (30%) calc for $[M - COOH]^-$ 138.938, where M = $As(CH_2COOH)O_3H_2$.

2.4. Synthesis of arsenoacetic acid $(AsCH_2COOH)_n$

Arsenoacetic acid was prepared based on the synthesis by Palmer [6]. Sodium arsonoacetate (12.5 g, 50 mmol) was added to a cold solution of conc. H_2SO_4 (22.5 mL), H_3PO_2 (47.6 mL, 50% in H_2O) and H_2O (100 mL). It was left to stand at room temperature under an N_2 atmosphere for three days. The orange precipitate was filtered under nitrogen, washed with water, and dried *in vacuo* over conc. H_2SO_4. The filtrate was allowed to stand under N_2 for another two days, and a second crop was obtained. Combined fractions were 4.70 g, 70%. Found: C, 17.40; H, 2.26%; $(AsCH_2COOH)_n$ requires: C, 17.93; H, 2.26%. ^{1}H NMR: [Pyridine-d_5] δ 3.59 (s, CH_2) ppm; $^{13}C\{^1H\}$ NMR: δ 26.9 (s, CH_2), 174.1 (s, COOH) ppm. IR: (cm^{-1}) 3410(m, br) 2944(m, br) 2638(m) 2558(w) 1681(vs) 1438(m) 1287(s) 1132(m) 1096(m) 948(m) 824(w) 766(w) 658(w) 491(m). ESI-MS: [1:1 CH_3CN:H_2O] (with the addition of a small drop of pyridine) m/z 1472.275 (<1%) calc for $[(AsR)_{11} - H]^-$ 1472.276; 1338.342 (<1%) calc for $[(AsR)_{10} - H]^-$ 1338.341; 1204.409 (1%) calc for $[(AsR)_9 - H]^-$ 1204.406; 1070.473 (<1%) calc for $[(AsR)_8 - H]^-$ 1070.471; 952.528 (4%) calc for $[(AsR)_7O - H]^-$ 952.531; 876.517 (<1%) calc for $[(As_7R_6) - 2H]^-$ 876.515; 802.602 (100%) calc for $[(AsR)_6 - H]^-$ 802.602; 742.581 (2%) calc for $[(As_6R_5) - 2H]^-$ 742.580; 668.667 (50%) calc for $[(AsR)_5 - H]^-$ 668.667; 608.646 (8%) calc for $[As_5R_4 - 2H]^-$ 608.646; 534.732 (13%) calc for $[(AsR) - H]^-$ 534.732; 474.711 (6%) calc for $[As_4R_3 - 2H]^-$ 474.711; 400.798 (12%) calc for $[(AsR)_3 - H]^-$ 400.797.

2.5. X-ray crystal structure determinations

Crystals were obtained by slow evaporation of an aqueous solution for **3** and by cooling a saturated pyridine solution from room temperature to 4 °C for **4**. Data were collected on a Bruker Apex II CCD diffractometer with Mo-Kα X-rays. Corrections for absorption were carried out using a multi-scan procedure. Structures were solved using the SHELXS97 program [12] and refined on F_o^2 with SHELXL97 [12] operating under the WinGx interface [13]. Analysis of hydrogen bonding was performed with Mercury [14]. Diagrams were generated with ORTEP-III [15] and CrystalMaker [16]. Crystal data and refinement details are summarized in Table 1.

3. Results and discussion

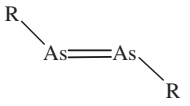
3.1. Syntheses and characterisation

The syntheses are summarised in Scheme 1. Preparation of barium arsonoacetate was carried out using the Meyer reaction [9], as modified by Palmer [6] wherein an alkaline solution of As_2O_3 was reacted with $ClCH_2COOH$, the product then being precipitated as the barium salt, $Ba_3[As(CH_2COO)O_3]_2$. This was readily converted to the more soluble sodium salt $Na_3[As(CH_2COO)O_3]$ by stirring in an aqueous solution of Na_2SO_4 and removing $BaSO_4$ by filtration.

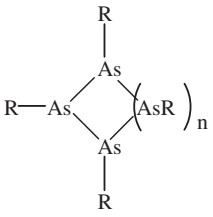
The barium salt was also the precursor for arsonoacetic acid **3**. The original method reported by Palmer in which $Ba_3[As(CH_2COO)O_3]_2$ was reacted with H_2SO_4, followed by recrystallization from EtOH gave reasonable yields of the free acid [6]. However, an alternative route [10,11] involving stirring a suspension of

Table 1
Crystal data and refinement details.

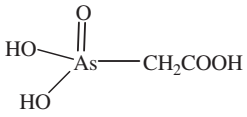
Compound	$As(CH_2COOH)O_3H_2$	$As_6(CH_2COOH)_6\cdot 6C_5NH_5$
Formula	$C_2H_5AsO_5$	$C_{42}H_{48}As_6N_6O_{12}$
M_r	183.98	1278.38
T (K)	121(2)	90(2)
Crystal system	Orthorhombic	Triclinic
Space group	$P2_12_12_1$	P-1
a (Å)	6.0904(3)	10.1456(1)
b (Å)	7.7557(4)	11.6233(1)
c (Å)	10.4713(5)	12.4298(2)
α (deg)	90	113.948(1)
β (deg)	90	92.378(1)
γ (deg)	90	106.716(1)
V (Å^3)	494.62(4)	1261.85(3)
Z	4	1
ρ (g cm^{-3})	2.471	1.682
μ (mm^{-1})	6.80	3.989
Size (mm^3)	0.40 × 0.56 × 0.60	0.29 × 0.20 × 0.17
F (000)	360	636
θ_{max} (deg)	32.6	28.1
Refln collected	13,348	37,809
$T_{max,\ min}$	0.1718, 0.1057	0.5504, 0.3908
Unique reflns (R_{int})	1764(0.0548)	6128(0.0384)
R_1 [$I > 2\sigma(I)$]	0.0190	0.0221
wR_2 (all data)	0.0507	0.0466
GOF on F^2	1.188	1.035
Final Δe (e Å^{-3})	+0.38/−1.20	+0.45/−0.30



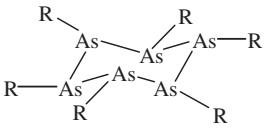
1a R = 3-amino-4-hydroxyphenyl
1b R = CH_2COOH



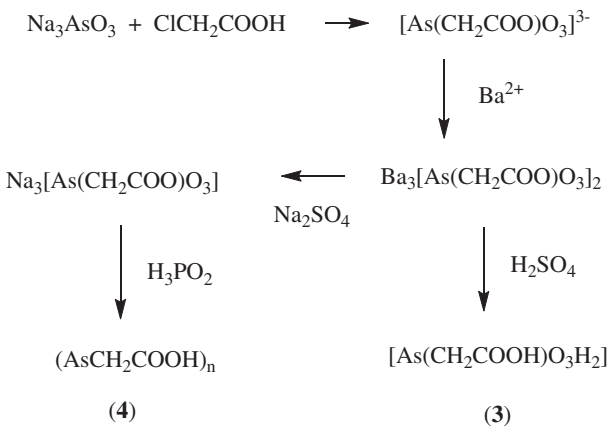
2 R = 3-amino-4-hydroxyphenyl
n = 0 - 5



3



4 R = CH_2COOH



Scheme 1.

$Ba_3[As(CH_2COO)O_3]_2$ with an ion-exchange resin in its acid form was more convenient and gave better yields of pure $As(CH_2COOH)O_3H_2$, **3**. This was fully characterised by elemental analysis and by NMR spectroscopy which showed singlet signals at δ 3.73 for CH_2 in the ^1H and δ 39.3 (CH_2) and 168.0 (*C*OOH) in the ^{13}C spectra. ESI-MS of an aqueous solution gave the expected ions in negative ion mode; $[M - H]^-$ was the dominant peak, with others arising from aggregates ($[2M - H]^-$ and $[3M - H]^-$) and from condensation processes ($[2M - H_2O - H]^-$ and $[3M - H_2O - H]^-$). One other significant peak of interest corresponded to $[M - CO_2 - H]^-$, arising from decarboxylation of the acid. This unusual fragmentation under mild electrospray conditions can be understood from the presumed structure of the resulting ion, $[H_2O_3As{=}CH_2]^-$ which is an arsenic ylide so would have some stability. The crystal structure of **3** was determined by X-ray methods, see below.

The As(I) compound arsenoacetic acid was prepared by reduction of $Na_3[As(CH_2COO)O_3]$ with H_3PO_2 at room temperature under a nitrogen atmosphere [6]. This gave an insoluble orange powder of the crude product which appeared pure from elemental analysis and spectroscopic data. However, the pure acid is pale yellow, so the orange colour indicates some minor component which could not be identified. The solid arsenoacetic acid is readily oxidised and even when stored under nitrogen it slowly darkens in colour. The compound is not very soluble in common solvents so NMR spectra were recorded in pyridine-d_5 to give signals at δ 3.59 (^1H, CH_2) and δ 26.9 and 174.1 (^{13}C, CH_2 and *C*OOH respectively). Although the mass spectral studies (see below) show that the acid contains a range of rings, $(AsCH_2COOH)_n$, there was no apparent splitting of the NMR peaks, suggesting that the resonance frequencies of the {$AsCH_2COOH$} group are insensitive to its ring size.

The main region of the ESI-MS of arsenoacetic acid in MeCN:-H_2O:pyridine (1:1:0.1) is shown in Fig. 1, and peaks and full assignment are listed in Section 2.4. The main peaks are unambiguously assigned as $[(RAs)_n - H]^-$ for $n = 3$–11, R = CH_2COOH, which are undoubtedly derived from the corresponding cyclic species. Relative intensities suggest that the abundances are in the order $n = 6 > 5 > 4 > 3$ with others only very minor. Other peaks present were from a series $[As_mR_{m-1} - 2H]^-$ for $m = 4$–7. It is not apparent what the structure of these minor arsenic-rich species might be, but are possibly responsible for the orange colour of the sample. One other significant peak that consistently showed is $[(AsR)_7O - H]^-$ which is presumably a cyclic compound with seven As and one O making up the ring. While this is not unexpected, the equivalent oxygenated rings are not seen for any other nuclearities.

Note that the smaller ring sizes do not arise from fragmentation of larger ones in the mass spectrometer. Relative intensities of

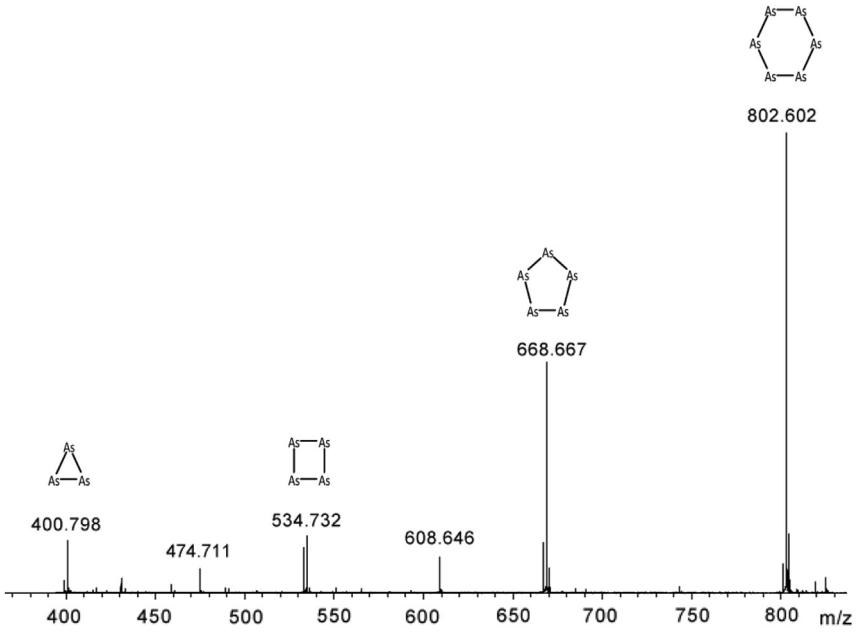


Fig. 1. An ESI-MS (−ve ion mode) of arsenoacetic acid, $(AsCH_2COOH)_n$ in MeCN:H_2O:pyridine (1:1:0.1) in the m/z 350–850 range. The peaks assigned to $[(RAs)_n - H]^-$ for $n = 3$–6 are indicated. The peaks at m/z 608.646 and 474.711 match $[(R_{m-1}As_m) - 2H]^-$ for $m = 5$ and 4 respectively but are of unknown structure and probably arise from impurities.

peaks remain constant under a range of conditions for any given sample, and when fragmentation does commence under very high exit-voltage conditions, the processes do not generate different ring sizes. Rather extrusion of $\{R_2As\}$ and loss of $\{CO_2\}$ occurs amongst other complicated pathways. Interconversion of ring sizes was also shown not to occur in MS–MS studies of Salvarsan rings in our earlier study [4].

These ESI-MS results clearly show that, as with most other organo-arsenic(I) compounds [3–5], arsenoacetic acid exists as a mixture of As_n rings, with the hexamer and pentamer the most abundant. There can no longer be any justification for formulating arsenoacetic acid as the diarsene **1b**.

The main features in IR spectra of all the compounds examined could be readily assigned, based on the literature [17]. The barium and sodium salts of arsonoacetic acid were similar, as expected. Broad O–H stretches around 3300–3400 cm^{-1} are associated with lattice water and possibly with incompletely ionised acid groups. A distinctive band for each at 2400 cm^{-1} can be ascribed to either overtones [18] or more likely to –OH stretching under strong H-bonding conditions [19]. The carboxylate C=O stretch is lower for the Ba^{2+} salt (1582 cm^{-1}) than for the Na^+ example (1601 cm^{-1}). Other major peaks are around 1400 cm^{-1} (CH_2 bending), 1260 cm^{-1} (C–O–H coupled stretch), 1100 cm^{-1} (C–C stretch) and 950 cm^{-1} (O–H deformation). The As–O peaks will be amongst the strong peaks in the 700–890 cm^{-1} region, which is more clearly resolved for the Na^+ salt. The As–C stretch gives rise to the peaks at 434 cm^{-1} (Na^+) and 419 cm^{-1} (Ba^{2+}).

For the arsonoacetic acid **3** the O–H stretching region from 3500 to 2300 is extremely broad, as expected given the extensive strong H-bonding network found in the crystal structure determination. The C=O stretch at 1688 cm^{-1} is at higher frequency compared with the equivalent in the Ba^{2+} and Na^+ salts, indicating a non-ionised carboxylic acid group. The strong As–O peaks are around 890 and 785 cm^{-1}, and the As–C stretch at 423 cm^{-1}.

For the arsenoacetic acid, the IR spectrum is much simpler. The O–H stretching region is again very broad, from 3400 to 2600 cm^{-1}, consistent with the extensive H-bonding that would be expected for the solid. The C=O stretch at 1681 cm^{-1} is similar to that for the arsonoacetic acid. The C–O–H coupled stretch at 1287 cm^{-1} and the C–O–H deformation at 948 cm^{-1} are relatively more intense than for the salts. There are no intense peaks between 700 and 900 cm^{-1}, consistent with the absence of As=O and As–O groups. The As–C stretch at 491 cm^{-1} is at higher frequency than observed for the arsonoacetic and for the salts.

In an attempt to purify the arsenoacetic acid, a concentrated solution in pyridine was cooled and produced some pale-yellow crystals suitable for X-ray crystal structure analysis. As discussed below, these proved to be of the hexamer, which fractionally crystallised from the mixture as the pyridine solvate. Attempts to grow crystals of the other ring sizes were not successful.

3.2. *X-ray crystal structures of **3** and **4***

The structure of arsonoacetic acid is illustrated in Fig. 2, with selected bond parameters listed in the caption. The compound is isomorphous with the corresponding phosphonoacetic acid [20] and the structures differ only in the longer As–O, As=O and As–C for **3** as a consequence of the larger size of As compared with P. The arsenic atom is close to tetrahedral, linked to three O atoms and to the acetic acid moiety by an As–C bond. The H atoms on O(1) and O(2) were located in the refinement, leaving O(3) as the formally doubly-bonded one. However, all the As–O distances are very similar because there is extensive H-bonding between molecules. As=O(3) acts as a double H-acceptor, from a carboxylate O–H(4) of one molecule and from an As–O–H(1) of another. The carboxylate C=O acts as an acceptor towards the As–O–H(2) of an adjacent molecule. The phosphonoacetic acid shows the same lattice interactions [20], though in this case the P=O bond remains significantly shorter than the P–OH ones.

The structure of the arsenoacetic acid hexamer **4** as the pyridine solvate is shown in Figs. 3 and 4. Molecules lie on a crystallographic inversion centre and consist of a puckered, cyclic As_6 ring with a chair conformation. Each As carries a $-CH_2COOH$ group in an equatorial position. Structurally characterised $(RAs)_6$ molecules previously reported are those with R = Ph, *p*-tolyl and *p*-$MeOC_6H_4$ [5a–c] so the present example is the first hexamer with a non-aromatic substituent.

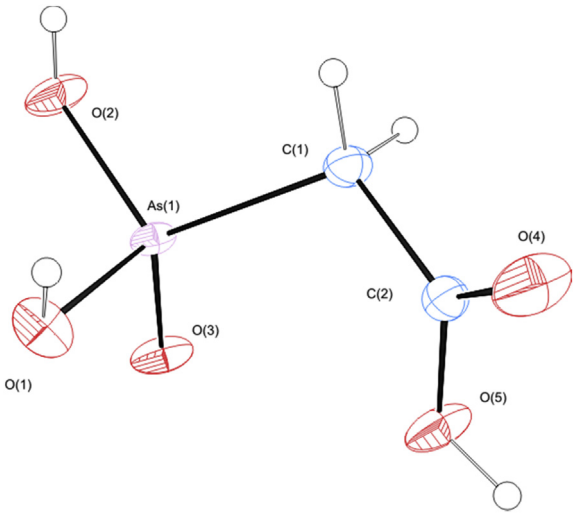


Fig. 2. The molecular structure of arsonoacetic acid, **3**. Selected bond parameters are bond lengths (Å): As(1)–O(1) 1.7013(13), As(1)–O(2) 1.6461(12), As(1)–O(3) 1.7072(13), As(1)–C(1) 1.9185(17); bond angles (deg): O–As–O (av.) 107.0(1)°, O–As–C (av.) 111.9(1)°.

Other $(RAs)_n$ rings with a sp^3-C substituent for which structures are known are either pentamers (R = CH_3, CH_2SiMe_3) or tetramers (R = ^{t}Bu, CF_3) [5]. For **4** the As–As bond lengths average 2.4594(3) which is essentially the same as in other published examples. However, the ring in **4** is more puckered than that in $(PhAs)_6$, with As–As–As angles averaging 88.61(1)° for **4** and 91.0° for the aryl example. The C–As–As bonds are 98.88(5)°, so the As atoms are by no means tetrahedral, with the lone pair having a strong steric effect.

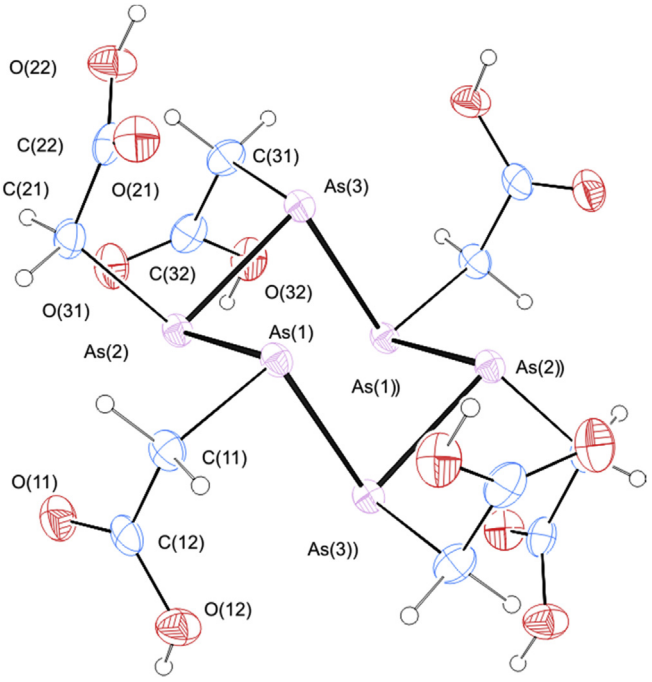


Fig. 3. The structure of a molecule of the arsenoacetic acid hexamer. Selected bond parameters are bond lengths (Å): As(1)–As(2) 2.4566(3), As(2)–As(3) 2.4589(3), As(1)–As(3)′ 2.4628(3), As–C (av.) 1.999(2); bond angles (deg): As(1)–As(2)–As(3) 89.228(9), As(2)–As(3)–As(1)′ 87.856(9), As(2)–As(1)–As(3)′ 88.753(8), C–As–As (av.) 98.88(5).

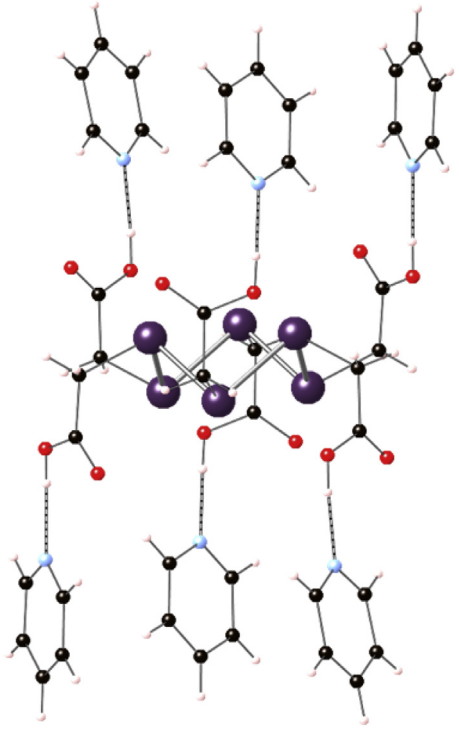


Fig. 4. A representation of the structure of $(AsCH_2COOH)_6 \cdot 6C_5H_5N$, showing the H-bonding interactions between the pyridine molecules and the carboxyl groups. Average distances (Å) are: O–H 0.85(3), H···N 1.77(3), O···N 2.624(2).

The acetic acid moieties are arranged so they alternate above and below the As_6 ring, giving idealised C_{3v} symmetry. This allows them to form H-bonds to six pyridine molecules trigonally arranged above and below, as shown in Fig. 4. The carboxyl H atoms were located in the X-ray determination so the structure is better described as COOH groups H-bonding to pyridine, rather than COO^- groups acting as H-acceptors from pyridinium cations, but the H···N interactions are strong as indicated by distances that are towards the shorter end of the range found for other systems [21].

4. Conclusion

Arsonoacetic acid has the same crystal structure as the phosphorus equivalent, phosphonoacetic acid. On reduction this gives the As(I) species arsenoacetic acid which is a mixture of $(AsCH_2COOH)_n$ rings with the $n = 6$ and 5 the main species. The hexamer contains an As_6 ring which is strongly puckered in a chair conformation, with the substituents in equatorial sites.

Acknowledgements

We thank Dr Jan Wikaira, University of Canterbury, and Dr Tania Groutso, University of Auckland, for collection of X-ray intensity data sets.

Appendix A. Supplementary material

CCDC 939836 and 939837 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.07.056.

References

[1] (a) P. Ehrlich, A. Bertheim, Ber. Dtsch. Chem. Ges. 45 (1912) 756;
(b) S. Riethmiller, Bull. Hist. Chem. 24 (1999) 28;
(c) F. Stern, Angew. Chem. Int. Ed. 43 (2004) 4254;
(d) A. Lykknes, L. Kvittingen, J. Chem. Educ. 80 (2003) 497;
(e) N.C. Lloyd, H.W. Morgan, B.K. Nicholson, R.S. Ronimus, S. Riethmiller, Chem. N. Z. 69 (2005) 24.

[2] (a) A.S. Levinson, J. Chem. Ed. 54 (1977) 98;
(b) A.H. Cowley, J.E. Kiduff, J.G. Lasch, S.K. Mehrotra, N.C. Norman, M. Pakulski, B.R. Whittlesey, J.L. Atwood, W.E. Hunter, Inorg. Chem. 23 (1984) 2582;
(c) B. Twamley, C.D. Sofield, M.M. Olmstead, P.P. Power, J. Am. Chem. Soc. 121 (1999) 3357;
(d) A.H. Cowley, N.C. Norman, M. Pakulski, J. Chem. Soc. Dalton Trans. (1985) 383;
(e) M. Bousikhane, H. Gomitzka, J. Escudie, H. Ranaivonjatovo, J. Organomet. Chem. 619 (2001) 275.

[3] L.R. Smith, J.L. Mills, J. Organomet. Chem. 84 (1975) 1.

[4] N.C. Lloyd, H.W. Morgan, B.K. Nicholson, R.S. Ronimus, Angew. Chem. Int. Ed. 44 (2005) 941.

[5] (a) $(PhAs)_6$: K. Hedberg, E.W. Hughes, J. Waser Acta Crystallogr. 14 (1961) 369;
A.L. Rheingold, P.J. Sullivan, Organometallics 2 (1983) 327;
(b) $(p\text{-}MeC_6H_4As)_6$, $(p\text{-}MeC_6H_4As)_5$ and $(PhAs)_5$: A.L. Rheingold, O.M. Kekia, J.B. Strong Main Group Chem. 2 (1997) 31;
(c) $(p\text{-}MeOC_6H_4As)_6$: M.B.L. Marx, H. Pritzkow, B.K. Keppler Z. Anorg. Allg. Chem. 623 (1997) 75;
(d) $(Me_3SiCH_2As)_5$: R.L. Wells, C.Y. Kwag, A.P. Purdy, A.T. McPhail, C.G. Pitt Polyhedron 9 (1990) 319;
(e) $(CH_3As)_5$: J.H. Burns, J. Waser J. Am. Chem. Soc. 79 (1957) 859;
(f) $(Bu^tAs)_4$: O. Mundt, G. Becker, H.J. Wessely, H.J. Breunig, M. Kischkel Z. Anorg. Allg. Chem. 486 (1982) 70;
(g) $(CF_3As)_4$: N. Mandel, J. Donohue Acta Crystallogr. D27 (1971) 476;
(h) $(MesitylAs)_4$: A.J. Roening, J.J. Davidson, S.N. MacMillan, J.M. Tanski, R. Waterman Dalton Trans. (2008) 4488.

[6] C.S. Palmer, J. Am. Chem. Soc. 45 (1923) 3023.

[7] The Merck Index, thirteenth ed., 2001. Whitehouse Station, New Jersey, USA.

[8] (a) B.J. Bremmer, L. Sonnabend, US Patent 3519476, 1970.
(b) W. Tarello, N. Riccieri, European Patent EP0911031, 2004. (c) W. Tarello, Comp. Immunol. Microbiol. Infect. Dis. 24 (2001) 57.

[9] G. Meyer, Ber. Dtsch. Chem. Ges. 16 (1883) 1439.

[10] T.A. Rozovskaya, V.O. Rechinsky, R.S. Bibilashvili, M.Y. Karpeisky, N.B. Tarusova, R.M. Khomutov, H.B.F. Dixon, Biochem. J. 224 (1984) 645.

[11] M.J. Sparkes, H.B.F. Dixon, Microbiology 141 (2008) 726.

[12] G.M. Sheldrick, SHELX97, Programs for Crystal Structure Analysis, University of Gottingen, Germany, 1997;
G.M. Sheldrick, Acta Crystallogr. A64 (2008) 112.

[13] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.

[14] Mercury V2.4, Cambridge Crystallographic Data Centre, Cambridge, UK, 2011.

[15] ORTEP-III L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.

[16] CrystalMaker 2.3.5, www.crystalmaker.com.

[17] L.D. Pettit, D. Turner, Spectrochim. Acta 24A (1968) 999.

[18] S. Bratoz, D. Hadzi, N. Sheppard, Spectrochim. Acta 8 (1956) 249.

[19] J.T. Braunholtz, G.E. Hall, F.G. Mann, N. Sheppard, J. Chem. Soc. (1959) 868.

[20] T. Lis, Acta Crystallogr. C53 (1997) 28.

[21] (a) J. Bernstein, M.C. Etter, L. Leiserowitz, in: H.-B. Bürgi, J.D. Duntitz (Eds.), Structure Correlation, VCH, Weinheim, 1994 (Chapter 11);
(b) T. Steiner, Angew. Chem. Int. Ed. 41 (2002) 48.