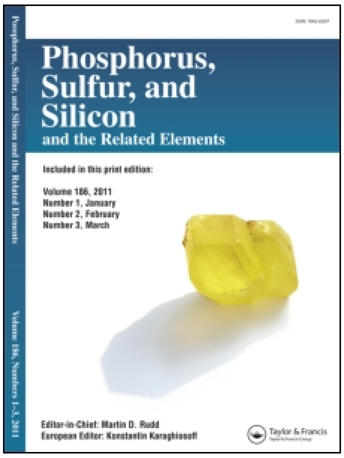

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SYNTHESIS, REACTIVITY AND STRUCTURES OF CYCLIC ARSENITES WITH AN AS BOND

K. C. Kumara Swamy[a]; Musa A. Saida[a]; Michael Veith[b]; V. Huch[b]
[a] School of Chemistry, University of Hyderabad, Hyderabad, A. P., INDIA [b] Anorganische Chemie, Universität des Saarlandes, Saarbrücken, Germany

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SYNTHESIS, REACTIVITY AND STRUCTURES OF CYCLIC ARSENITES WITH AN N→AS BOND

K. C. KUMARA SWAMY[a*], MUSA A. SAID[a], MICHAEL VEITH[b] and V. HUCH[b]

[a]*School of Chemistry, University of Hyderabad, Hyderabad- 500046, A. P. INDIA and* [b]*Anorganische Chemie, Universität des Saarlandes, 66041- Saarbrücken, Germany*

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Synthesis and X-ray structures of the cyclic arsenites (NC_9H_6O)As(2,2′-OC_6H_4-C_6H_4O) (**1**) and (NC_9H_6O)As[(O-2,4-(*t*-bu)$_2C_6H_2$)$_2CH_2$] (**2**) are described. Compound **1** crystallizes in the monoclinic space group $P2_1$ with $a = 10.469$ (7)Å, $b = 7.126$ (4)Å, $c = 11.837$ (6)Å, $\beta = 95.14$ (5)°, V = 879.5 (9) Å^3, $Z = 2$. Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.320$ (6)Å, $b = 12.749$ (7)Å, $c = 14.257$ (8)Å, $\alpha = 97.21$ (4), $\beta = 97.21$ (4), $\gamma = 102.62$ (4)°, V = 1732 (2) Å^3, Z = 2. Both the compounds exhibit intramolecular N →As coordination with a distorted trigonal bipyramidal geometry around arsenic; the coordinated nitrogen is in the apical position and the stereochemically active lone pair on arsenic is located approximately in the equatorial plane. The hydrolytic behaviour of **1, 2** and (NC_9H_6O)As($OCH_2CMe_2CH_2O$) (**4**) is compared with that of the corresponding phosphorus analogues.

Keywords: Cyclic arsenites; internal coordination; X-ray structures

INTRODUCTION

Structural and conformational studies on ring systems of the types **I-III** wherein arsenic is a part of a *six- or higher membered rings* are scanty.[1–4] We have recently reported the structures of two compounds **IV** and **V** in which arsenic is connected to three other atoms as in **I**.[5] Our attempts to obtain structurally characterizable compounds of type **III** have so far been

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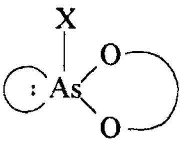
[*] Address for correspondence: Dr. K. C. Kumara Swamy, School of Chemistry, University of Hyderabad, Hyderabad- 500 046, India. e-mail: kckssc@uohyd.ernet.in Fax: +91–40–3010120.

unsuccessful. In this paper we report the synthesis of compounds **1–3** of type **II**; hydrolysis of these as well as the arsenane **4** is compared to the corresponding phosphorus analogues. X-ray structures of **1** and **2**, which represent the first examples of internally coordinated cyclic arsenites with seven- and eight-membered rings, are also described. Compounds **1–4** can be considered to be 10-electron systems (on arsenic) analogous to pentacoordinated arsoranes.



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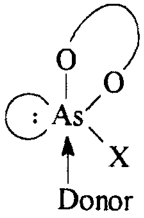

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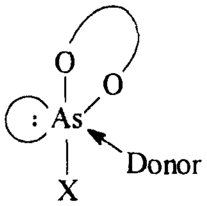

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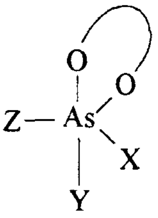

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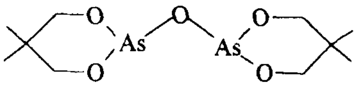

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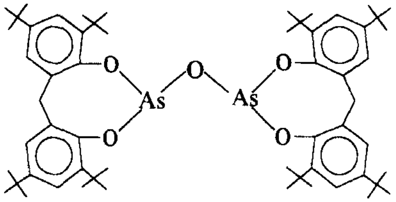

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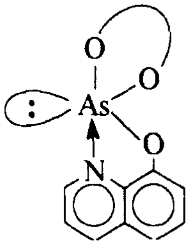
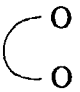




= 2, 2' - OC_6H_4 - C_6H_4O (**1**)

= {O - 2, 4 -(*t*-Bu)$_2C_6H_2$}$_2C_6H_2$ (**2**

= $O_2C_6H_4$ (**3**)

= $OCH_2CMe_2CH_2O$ (**4**)

EXPERIMENTAL

Chemicals were purchased from Aldrich/ Fluka or local manufacturers; they were purified according to standard procedures. All operations, unless otherwise stated, were performed under dry nitrogen. ^1H and ^{13}C NMR spectra were recorded on a Bruker 200 MHz or a JEOL 100 MHz spectrometer using $CDCl_3$ (or C_6D_6) solutions with shifts referenced to TMS ($\delta = 0$). IR spectra were recorded on JASCO FT/ IR-5300 spectrophotometer. Elemental analyses were carried out on a Perkin Elmer 240C CHN analyser. Synthesis of **4** {IR (800–400cm^{-1}): 781 (vs), 742 (s), 710 (s), 640 (s), 613 (s), 580 (m), 552 (vs), 525 (w), 461 (w)} as well as its phosphorus analogue $(NC_9H_6O)P(OCH_2CMe_2CH_2O)$ (**5**) has already been described.[6] The procedure for the preparation of compound **1** is described below; compounds **2** and **3** were prepared analogously on a similar scale.

a) Preparation of the cyclic arsenile $(NC_9H_6O)As(2,2'\text{-}OC_6H_4\text{-}C_6H_4O)$ (1)

To the chloroarsenite $ClAs(2,2'\text{-}OC_6H_4\text{-}C_6H_4O)$[5,7] (0.762 g, 2.59 mmol) in dry benzene (30 mL) [Caution: Benzene is a suspected carcinogen] a mixture of 8-hydroxy quinoline (0.375 g, 2.59 mmol) and triethylamine (0.5 mL) in dry benzene (20 mL) was added dropwise. The reaction mixture was stirred for 10h, filtered and the solvent was removed. The residue was crystallized from dichloromethane-hexane (1:2) mixture. Yield: 0.79 g (76 %); m.p. 138°C. IR (800–400cm^{-1}): 789 (w), 774 (vs), 754 (vs), 714 (m), 635 (m), 606 (s), 577 (w), 536 (m), 521, 498, 484, 468 (all w), 444 (m) {*cf.* IR (800–400cm^{-1}) of $(NC_9H_6O)P(2,2'\text{-}OC_6H_4C_6H_4O)$ (**6**): 780 (vs), 750 (s), 706 (s), 680 (m), 600 (s), 554 (m), 519 (m), 494 (w), 465 (m), 432 (w)}. ^1H NMR: δ 7.0–8.9 (*H*(Ar)). ^{13}C NMR: δ 110.0–152.3 (*C*(Ar)). Anal. Calc. for $C_{21}H_{14}AsNO_3$: C, 62.52; H, 3.49; N, 3.47. Found: C, 62.40; H, 3.60; N, 3.56.

b) The cyclic arsenite $(NC_9H_6O)As[(O\text{-}2,4\text{-}(t\text{-}bu)_2C_6H_2)_2CH_2]$ (2)

Recrystallized from dichloromethane-hexane (1:4) mixture. Yield: 64 %; m.p. 208°C. IR (800–400cm^{-1}): 785 (m), 754 (s), 737 (vs), 695 (w), 646 (w), 631 (w), 602 (w), 602 (w), 583 (w), 561 (s), 534 (s), 494 (w), 459 (w), 440 (w). ^1H NMR: δ 1.29 (s, 18H, CH_3), 1.33 (s,18H, CH_3), 4.06 (AB quartet, 2H, C*H*$_2$), 7.15–8.85 (m, 10H, *H*(Ar)). ^{13}C NMR: δ 30.0 (*C*H$_3$), 31.8 (*C*H$_2$), 34.4 (*C*CH$_3$), 35.1 (*C*CH$_3$), 110.0–154.6 (many lines, *C*(Ar)). *Anal.* Calc. for $C_{38}H_{48}AsNO_3$: C, 71.12; H, 7.54; N, 2.18. Found: C, 71.10; H, 7.45; N, 2.45.

c) The cyclic arsenite (NC_9H_6O)As(*o*-$O_2C_6H_4$) (3)

Recrystallized from dichloromethane-hexane mixture. Yield: 40 %; m.p. 210°C. IR (800–400cm^{-1}): 798 (vs), 780 (m), 739 (vs), 662 (s), 629 (vs), 552 (w), 530 (w), 446 (w). ^{1}H NMR: 6.7–9.0 (*H*(Ar)) Anal. Calc. for $C_{15}H_{10}AsNO_3$: C, 55.05; H, 3.06; N, 4.28. Found: C, 55.78, H, 3.14; N, 4.36.

d) Hydrolysis studies

Hydrolysis of **1–5** was conducted in dichloromethane or THF solution in air by adding three mole equivalents of water. Compound **4** gave initially [$OCH_2CMe_2CH_2O$)As]$_2$O (**IV**, ^{1}H NMR)[5] which underwent further hydrolysis to give As_2O_3, quinol and the diol over a period of a few days; the corresponding phosphorus compound (NC_9H_6O)P($OCH_2CMe_2CH_2O$) (**5**) gave the salt [HNC_9H_6O]$^+$[P(H)(O)(O$^-$)($OCH_2CMe_2CH_2OH$)] (**6**, viscous liquid). Compound **6**: Yield: > 95%). ^{1}H NMR: δ 0.87 (s, 6H, *C*H$_3$), 3.40 (s, 2H, *C*H$_2$), 3.78 (d, ^{3}J(P-H) = 10 Hz, 2H, C*H*$_2$OP), 7.05 (d, ^{1}J(P-H) = 645 Hz, 1H, P-*H*) ^{13}C NMR: δ 21.4 (s, 1C, *C*H$_3$), 37.0 (d, ^{3}J(P-C) = 5 Hz, *C*Me$_2$), 67.3 (s, 1C, *C*H$_2$), 69.2 (d, ^{2}J = 5 Hz, *C*H$_2$OP), 114.1, 117.5, 121.4, 129.5, 129.6, 122.5, 141.1, 145.0 and 151.0, (all *C*(Ar)) ^{31}P NMR: δ 5.6.

Compound **1** upon hydrolysis gave only As_2O_3, diol and 8-hydroxy quinoline (IR); the corresponding phosphorus compound **7** gave [HNC_9H_6O]$^+$[P(H)(O)(O$^-$) (OC_6H_4-C_6H_4OH)] (**8**) in 97% yield. M.p. 146°C. ^{1}H NMR: (DMSO-d$_6$): δ 6.78 (d, ^{1}J(P-H) = 640 Hz, 1H, P*H*), 6.70–8.90 (m, 14H, *H*(Ar)). ^{31}P NMR: δ 4.4. *Anal.* Calc. for $C_{21}H_{18}NO_5P$: C, 63.80; H, 4.56; N, 3.87. Found: C, 63.30; H, 4.46; N, 3.70.

X-ray structural analysis

Crystals suitable for X-ray work were obtained from dichloromethane-hexane. Data were collected on a Siemens four circle AED2 diffractometer after inserting the crystals inside a capillary. Details of data collection and structure determination are summarized in Table I. The structures were solved by conventional methods.[8] H-atoms were fixed by geometry; the nonhydrogen atoms were refined anisotropically.

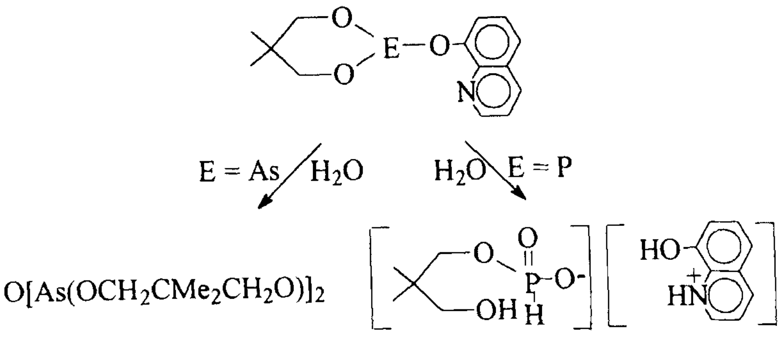
TABLE I Crystallographic data for **1** and **2**

Compound	**1**	**2**
Formula	$C_{21}H_{14}AsNO_3$	$C_{38}H_{48}AsNO_3$
fw	403.25	641.69
T(K)	293 (2)	293 (2)
Space group	$P2_1$	$P\bar{1}$
a/ Å	10.469 (7)	11.320 (6)
b/ Å	7.126 (4)	12.749 (7)
c/ Å	11.837 (6)	14.257 (8)
α/ °	-------	116.50 (3)
β/ °	95.14 (5)	97.21 (4)
γ/ °	--------	102.62 (4)
V/ $Å^3$	879.5 (9)	1737 (2)
Z	2	2
d_{calcd}, gcm^{-3}	1.523	1.227
μ, cm^{-1}	19.53	10.14
λ, Å	0.71073	0.71073
F(000)	408	680
Refl. collected	2518	4553
Obsd reflections (I > 2 σ (I))	2200	3527
Goodness of fit	1.078	1.031
Final R indices (I > 2 σ (I))	R1 = 0.0284 wR2 = 0.0717	R1 = 0.0348 wR2 = 0.0787

RESULTS AND DISCUSSION

Synthesis, stability and spectra

All the four compounds **1–4** can be readily prepared as crystalline solids in yields of 60–80% by treating the corresponding chloro precursor[5] with 8-hydroxyquinoline using triethylamine as a base. Compounds **1–4**, although stable under dry conditions, are hydrolyzed when moisture is present. Compound **1** hydrolyses to the previously reported oxo-bridged compound $[OCH_2CMe_2CH_2O)As]_2O$ **(IV)**[5] which upon further reaction with water leads to As_2O_3 and $HOCH_2CMe_2CH_2OH$. This feature contrasts with that of the phosphorus analogue $(NC_9H_6O)P(OCH_2CMe_2CH_2O)$ (**5**) which hydrolyzes to give the salt $[HNC_9H_6O]^+[P(H)(O)(O^-)(OCH_2CMe_2CH_2OH)]$ (**6**) (Scheme 1).[9] Compound **3**, although hydrolytically much more stable than **1**, gave only As_2O_3 and the diol upon hydrolysis; the analogous phosphorus compound $(NC_9H_6O)P(OC_6H_4C_6H_4O)$ (**7**) led to the salt $[HNC_9H_6O]^+[P(H)(O)(O^-)(OC_6H_4\text{-}C_6H_4OH)]$ (**8**). Hydrolytic behaviour of **2** and **4** is similar to that of **1**.



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SCHEME 1

The IR spectra of **1** and its phosphorus analogue **7** (which most likely lacks internal N→P coordination) show significant differences suggesting different geometries in the two compounds; however unambiguous assignment of the N→ As stretch after comparing the spectra has not been possible due to the presence of other bands.

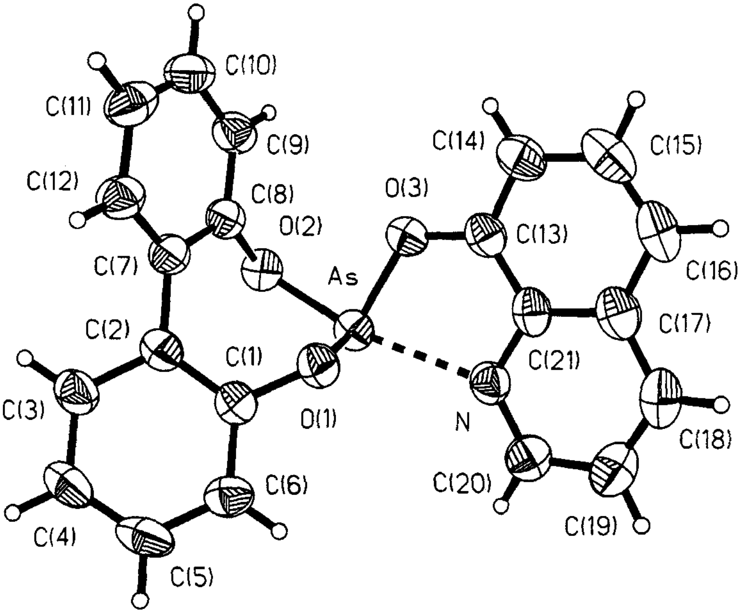


FIGURE 1 Molecular structure of **1**; H atoms not shown

For **3**, the two protons of the CH_2 group show up as an AB quartet in contrast to the tricoordinated compound $O[As\{O\text{-}2,4\text{-}(t\text{-}bu)_2C_6H_2\}_2]_2$ (**V**)[5] which exhibited a well-defined AX pattern [δ(A) = 3.50, δ(X) = 4.70, J(A-X) =13.0 Hz]. This is probably a result of the different ring conformations adopted by the eight membered ring in the two compounds (see below).

Structures

Both the compounds **1** and **2** show intramolecular N→As coordination [Figures 1 and 2]; the As-N bonds lengths [Table II] increase in the order **1** (2.434 Å) < **2** (2.534Å) < **4** (2.602Å (mean).[6] In the 2,2′- biphenoxy compound **1** having no electron donating substituent on the aromatic rings the arsenic is the most acidic leading to the strongest N→As interaction. However all these N→As bonds are weaker than those in $Me_3N \rightarrow AsCl_3$ (2.28Å)[10] or the hexacoordinated compound $(NC_9H_6O)As(OCH_2CMe_2CH_2O)_2$ (**VI**) (2.04 Å).[6]

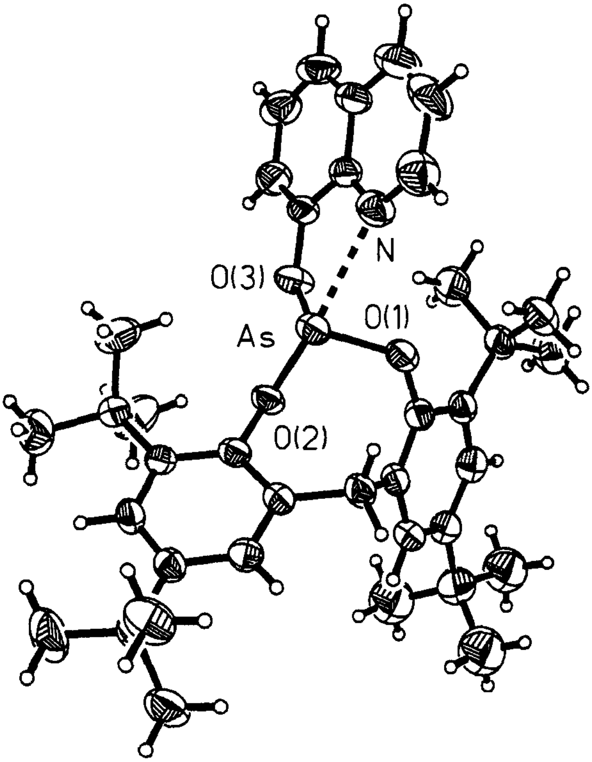


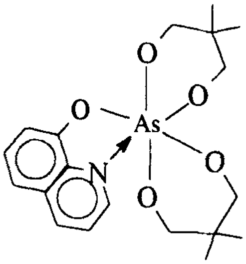
FIGURE 2 Molecular structure of **2**; H atoms not shown

The geometry in **1** and **2** can be considered to be approximately trigonal bipyramidal (TBP) with the lone pair of electrons on arsenic in an equatorial position and the nitrogen atom of the oxinate (instead of the oxygen) in an apical position. The apical As-O bonds are longer than the equatorial As-O bonds for the six-[6] or seven- or eight membered ring in **4**, **1** and **2** respectively as expected in a trigonal bipyramidal geometry for such systems. The N-As-O (apical) angle in **1**, **2** and **4** is 160–164° whereas in $Me_3N \rightarrow AsCl_3$[10] the N-As-Cl (axial) angle is 178.1° thus suggesting a greater distortion from the TBP structure for our compounds. Based on the dihedral angles (δ)[11] between the planes containing atoms (1,2,4) and (2,4,5) in the representation **(VII)** for compounds **1** (47.15°) and **2** (43.05°) a distortion of 11.2 % and 18.9 % from TBP ($\delta = 53.1°$) to square pyramidal ($\delta = 0$) geometry is estimated.

TABLE II Selected bond lengths (Å) and bond angles (°) for **1** and-**2** with esd's in parantheses

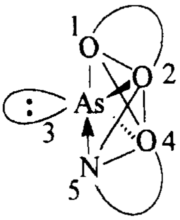
Compound 1			
As – O(1)	1.802 (2)	N – C(21)	1.357 (5)
As – O(2)	1.836 (3)	C(1) – C(2)	1.377 (5)
As – O(3)	1.814 (3)	C(2) – C(7)	1.475 (5)
O(1) – C(1)	1.388 (4)	C(7) – C(8)	1.416 (5)
O(2) – C(8)	1.370 (5)	C(13) – C(21)	1.409 (6)
O(3) – C(13)	1.360 (5)	As – N	2.434 (3)
O(1) – As – O(3)	95.89 (12)	C(8) – C(7) -C(2)	119.8 (3)
O(1) – As – O(2)	94.28 (11)	O(2) – C(8) – C(7)	118.8 (3)
O(2) – As – O(3)	88.95 (12)	O(3) – C(13) – C(21)	119.4 (3)
C(1) – O(1) – As	116.7 (2)	N – C(21) – C(13)	115.8 (3)
C(8) – O(2) – As	120.6 (2)	N – As – O(2)	163.80 (11)
C(13) – O(3) – As	123.6 (2)	N – As – O(1)	80.96 (11)
C(2) – C(1) – O(1)	120.4 (3)	N – As – O(3)	76.24 (11)
C(1) – C(2) – C(7)	121.2 (3)		
Compound 2			
As – O(1)	1.801 (2)	C(6) – C(7)	1.514 (4)
As – O(2)	1.817 (3)	C(7) – C(8)	1.514 (4)
As – O(3)	1.811 (2)	C(8) – C(9)	1.393 (4)
O(1) – C(1)	1.386 (4)	N – C(22)	1.350 (4)
O(2) – C(9)	1.402 (3)	C(14) – C(22)	1.409 (5)
O(3) – C(14)	1.369 (4)	As – N	2.534 (3)
C(1) – C(6)	1.395 (4)		
O(1) – As – O(2)	98.30 (10)	C(22) – N – As	101.9 (2)
O(1) – As – O(3)	99.60 (11)	C(1) – C(6) – C(7)	120.7 (3)
O(2) – As – O(3)	85.50 (11)	C(6) – C(7) – C(8)	118.7 (3)
O(1) – As – N	80.78 (10)	C(7) – C(8) – C(9)	121.9 (3)
O(2) – As – N	159.71 (10)	O(2) – C(9) – C(8)	118.0 (3)
O(3) – As – N	74.75 (11)	O(3) – C(14) – C(22)	119.7 (3)
C(1) – O(1) – As	124.7 (2)	O(1) – C(1) – C(6)	119.2 (3)
C(9) – O(2) – As	117.3 (2)	N – C(22) – C(14)	117.0 (3)
C(14) – O(3) – As	123.5 (2)		

Compound **1** is, to our knowledge, the first 'arsepin' to be structurally characterized. The conformation of the seven membered ring is that of a 'row-boat'; the atoms As, O(2), C(2) and C(1) form the base and are coplanar within 0.07 Å. The prow atom O(1) is displaced from this plane by ≈ 0.66 Å while the stern atoms C(7) and C(8) are displaced in the same direction by ≈ 1.0 Å.



(VI)

The 'arsocin' compound **2** exhibits a 'distorted tub' conformation with the atoms C(7), C(8), O(1) and As displaced from the mean plane containing C(9), O(2), C(1) and C(6) [maximum deviation ≤ 0.14 Å] by 0.97, 0.66, 0.35 and 1.28 Å respectively. This conformation, interestingly, differs from the 'symmetrical anti' conformation observed in **(V)**[5] and may be responsible for the difference in the ^{1}H NMR (CH_2 region) (see above).



VII

To summarize, in the cyclic arsenites with an oxinate substituent, the nitrogen of the oxinate will coordinate to the arsenic to lead to structures in which the lone pair on arsenic occupies an equatorial plane in a trigonal bipyramid; the hydrolytic pathway for these arsenites differs markedly from those of the corresponding cyclic phosphorus compounds.

Supplementary Material

Details on data collection/ refinement, atomic coordinates, bond distances and bond angles etc for **1** and **2** are deposited. CCDC ref. numbers 114217 and 114218.

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