Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	*y*	*z*	B_{eq}
Pd	0.22769 (3)	0.03259 (2)	0.07635 (2)	2.96 (1)
S1	0.2691 (1)	0.23810 (9)	0.03820 (6)	3.92 (4)
S2	0.2819 (1)	0.0172 (1)	−0.08529 (7)	4.34 (4)
P	0.20458 (9)	0.08660 (8)	0.23738 (6)	2.87 (3)
N1	0.1921 (3)	−0.1621 (3)	0.0864 (2)	3.3 (1)
N2	0.3654 (4)	0.4975 (4)	−0.1228 (3)	6.2 (2)
N3	0.4318 (5)	0.1614 (4)	−0.3049 (3)	6.6 (2)
C1	0.0679 (4)	−0.2152 (3)	0.1034 (3)	3.8 (1)
C2	0.0423 (4)	−0.3439 (4)	0.1094 (3)	4.7 (2)
C3	0.1472 (5)	−0.4206 (4)	0.0990 (3)	5.3 (2)
C4	0.2746 (5)	−0.3668 (4)	0.0813 (3)	5.3 (2)
C5	0.2951 (4)	−0.2381 (4)	0.0756 (3)	4.2 (2)
C6	0.3062 (3)	0.1797 (4)	−0.0749 (3)	3.6 (1)
C7	0.3488 (4)	0.2552 (4)	−0.1466 (3)	4.1 (2)
C8	0.3578 (4)	0.3889 (4)	−0.1329 (3)	4.6 (2)
C9	0.3929 (4)	0.2012 (4)	−0.2336 (3)	4.5 (2)
C21	0.1018 (3)	0.2225 (3)	0.2533 (2)	3.2 (1)
C22	0.1193 (4)	0.3032 (4)	0.3367 (3)	4.1 (2)
C23	0.0325 (5)	0.4000 (4)	0.3478 (3)	5.0 (2)
C24	−0.0705 (5)	0.4159 (4)	0.2765 (3)	5.0 (2)
C25	−0.0881 (4)	0.3361 (4)	0.1933 (3)	4.7 (2)
C26	−0.0018 (4)	0.2392 (3)	0.1814 (3)	3.8 (1)
C31	0.3727 (3)	0.1258 (3)	0.3043 (2)	3.0 (1)
C32	0.3914 (4)	0.1282 (4)	0.4053 (2)	3.8 (1)
C33	0.5215 (4)	0.1573 (4)	0.4532 (3)	4.6 (2)
C34	0.6330 (4)	0.1833 (5)	0.4019 (3)	5.2 (2)
C35	0.6158 (4)	0.1815 (5)	0.3028 (3)	5.5 (2)
C36	0.4863 (4)	0.1523 (4)	0.2536 (3)	4.2 (2)
C41	0.1235 (3)	−0.0355 (3)	0.3051 (2)	3.3 (1)
C42	−0.0114 (4)	−0.0319 (4)	0.3297 (3)	4.7 (2)
C43	−0.0706 (5)	−0.1316 (5)	0.3777 (4)	5.9 (2)
C44	0.0021 (5)	−0.2334 (5)	0.3981 (3)	5.7 (2)
C45	0.1341 (5)	−0.2383 (4)	0.3728 (3)	5.0 (2)
C46	0.1963 (4)	−0.1398 (4)	0.3269 (3)	4.0 (1)
N4	0.2955 (7)	0.4466 (6)	0.5565 (5)	10.1 (3)
C10	0.5278 (7)	0.5003 (6)	0.6547 (5)	8.6 (3)
C11	0.3964 (7)	0.4700 (6)	0.5997 (4)	7.2 (3)

Table 2. *Selected geometric parameters (Å, °)*

Pd—N1	2.082 (3)	P—C21	1.828 (3)
Pd—S1	2.288 (2)	N1—C1	1.341 (5)
Pd—S2	2.340 (1)	N1—C5	1.344 (5)
Pd—P	2.300 (1)	N2—C8	1.146 (6)
S1—C6	1.724 (4)	N3—C9	1.154 (5)
S2—C6	1.716 (4)	C6—C7	1.385 (5)
P—C31	1.816 (3)	C7—C8	1.414 (6)
P—C41	1.817 (3)	C7—C9	1.414 (6)
N1—Pd—S1	170.38 (8)	C6—S2—Pd	86.2 (1)
N1—Pd—S2	95.13 (8)	S2—C6—S1	110.6 (2)
N1—Pd—P	95.57 (8)	C6—C7—C8	121.2 (4)
S1—Pd—P	94.04 (4)	C6—C7—C9	121.0 (4)
S1—Pd—S2	75.35 (4)	C8—C7—C9	117.7 (3)
S2—Pd—P	167.89 (3)	N2—C8—C7	179.2 (5)
C6—S1—Pd	87.7 (1)	N3—C9—C7	177.4 (5)

Data were collected with a scan speed of < 5.49° min^{-1} and an ω-scan width of $(0.45 + 0.35\tan\theta)°$. The structure was solved by direct methods, the Pd atom being located in the *E* map and the remaining non-H atoms being deduced from successive difference Fourier syntheses. The structure was refined by full-matrix least-squares techniques. H atoms were positioned geometrically and not refined. All calculations were performed on a MicroVAX 3100 computer using the *TEXSAN* (Molecular Structure Corporation, 1987) program package.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *TEXSAN*. Program(s) used to solve structure: *MITHRIL* (Gilmore, 1983). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978).

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Lists of structure factors, least-squares-planes data, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1065). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1-Hydroxy-2,1λ^5-benzoxarsol-3-one Monohydrate

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Abstract

The stereochemistry around arsenic in the title compound, 1-hydroxybenz[*c*][1,2]oxarsol-3-one monohydrate, $C_7H_5AsO_3.H_2O$, is distorted trigonal bipyramidal, with the carboxylate O atom and the water molecule occupying apical positions, and the phenyl C atom, the hydroxyl group and the lone pair occupying equatorial positions. The formation of a bond between the As and

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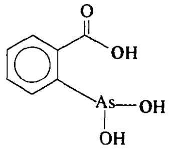
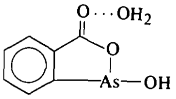
carboxylate O atoms leads to the formation of a five-membered ring fused with the phenyl ring. The water molecule forms a coordinate bond with arsenic(III). The earlier assignment of the title compound as *o*-carboxyphenylarsonous acid is thus incorrect.

Comment

The synthesis of *o*-carboxyphenylarsonous acid, (1*a*), was reported in the literature (Aeschlimann & McCleland, 1924). It was later shown (Parmar, Basra, Malhotra & Sandhu, 1980) using IR and thermal-analysis data that this compound exists as the cyclic compound 1-hydroxy-2,1λ^5-benzoxarsol-3-one monohydrate, (1*b*). To account for the decrease in the IR stretching frequency of the carbonyl group, it was proposed that the water molecule is hydrogen bonded to the carbonyl group. The structure determination of the title compound was undertaken in order to confirm the revised structure. The observation of a similar cyclization by interaction of the *o*-carboxylate O atom has already been observed in the case of 1-hydroxy-1,1-diphenyl-2,1λ^5-benzoxarsol-3-one (Bathla, Parmar, Saluja, Slawin & Williams, 1987), wherein two phenyl groups and a hydroxyl group are attached to arsenic(VI).



(1*a*)



(1*b*)

The stereochemistry about arsenic(III) is distorted trigonal bipyramidal, with the water molecule and the oxarsole ring O2 atom occupying the apical sites [O2—As···O4 171.5 (2)°] and the three equatorial positions occupied by the *o*-phenylene C atom, the hydroxyl group and the lone pair. All angles around arsenic(III) are comparable to the corresponding angles reported for $AsCl_3(NMe_3)_2$ (Webster & Keats, 1971), where a trigonal bipyramidal geometry has been proposed around arsenic(III). The As—O2 and As—O3 single-bond distances are 1.925 (4) and 1.763 (5) Å, respectively. The As—O2 distance is longer because of the strain of the five-membered ring. However, the bond is shorter than the corresponding ring As—O distance of 2.238 (2) Å observed in 1-hydroxy-1,1-diphenyl-2,1λ^5-benzoxarsol-3-one (Bathla *et al.*, 1987). In the latter, this bond is a resonance hybrid between a single and a coordinate bond, whereas in the case of the title compound, it is a single bond. If it were a coordinate bond, then the As—O distance would have been of the order 2.525 (5) Å (Parmar *et al.*, 1996). The As···O4 distance of 2.560 (5) Å in the title compound corresponds to an As^{III}···OH_2 coordinate bond (Fig. 1). A coordinate bond of 2.525 (5) Å has been observed between the As^{III} and carbonyl O atoms in the case of *o*-carboxyphenylmethylarsonous chloride (Parmar *et al.*, 1996).

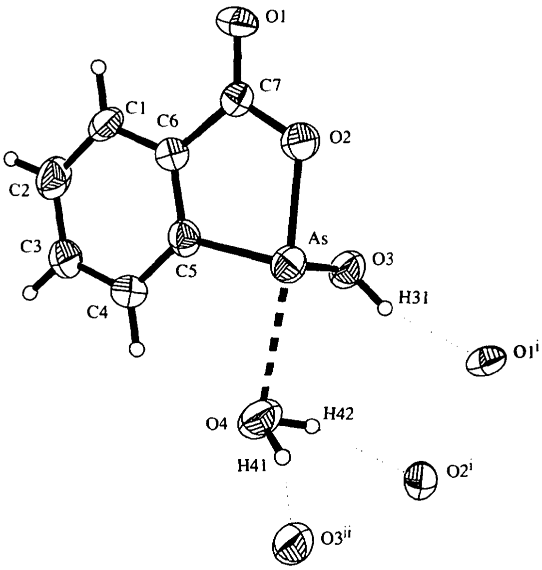
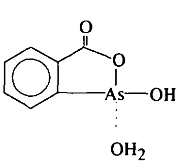


Fig. 1. A view of the title compound showing the labelling scheme and 50% displacement ellipsoids (*SHELXTL95*; Sheldrick, 1995)

All the O atoms are involved in extensive intermolecular hydrogen bonding in the molecule. Both the carboxylate O atoms act as hydrogen-bond acceptors and the water molecule acts as a hydrogen-bond donor, whereas the hydroxyl group behaves as a donor as well as an acceptor. An intermolecular hydrogen bond exists between the hydroxyl O3 group and the carbonyl O1^{i} atom, with an O3···O1^{i} distance of 2.70 (1) Å. The water molecule forms two intermolecular hydrogen bonds, one with the hydroxyl O3^{ii} atom at a distance of 2.79 (1) Å and the second with the carboxyl O2^{i} atom at a distance of 2.941 Å (symmetry codes as in Table 3). There is no inter- or intramolecular short contact between the carbonyl O atom and the coordinated water molecule. The observed decrease in the stretching frequency of the carbonyl group in the IR spectrum is therefore due to the intermolecular hydrogen bonding of the carbonyl O atom with the hydroxyl group and not with the water molecule as proposed earlier, *i.e.* (1*b*). The structure determination confirms that the compound originally referred to as *o*-carboxyphenylarsonous acid in the literature is actually the heterocyclic compound 1-hydroxy-2,1λ^5-benzoxarsol-3-one monohydrate, (1*c*).



(1*c*)

Experimental

The title compound was synthesized according to the method of Parmar *et al.* (1980).

Crystal data

$C_7H_5AsO_3.H_2O$
$M_r = 230.05$
Monoclinic
$P2_1/n$
$a = 5.1840\,(10)$ Å
$b = 15.569\,(2)$ Å
$c = 10.0530\,(15)$ Å
$\beta = 93.64\,(2)°$
$V = 809.7\,(2)$ Å^3
$Z = 4$
$D_x = 1.887$ Mg m^{-3}
$D_m = 1.87$ Mg m^{-3}
D_m measured by flotation in benzene/bromoform

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 3$–$20°$
$\mu = 4.167$ mm^{-1}
$T = 293\,(2)$ K
Prismatic
$0.30 \times 0.20 \times 0.20$ mm
Colourless

Data collection

Siemens *R*3*m*/*V* diffractometer
2θ–θ scans
Absorption correction: none
2872 measured reflections
1424 independent reflections
961 observed reflections $[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0610$
$\theta_{\text{max}} = 25.0°$
$h = -6 \rightarrow 6$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 11$
3 standard reflections monitored every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0442$
$wR(F^2) = 0.1037$
$S = 1.001$
1424 reflections
110 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0253P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} = 0.001$
$\Delta\rho_{\text{max}} = 0.393$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.475$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0041 (11)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
As	0.19062 (13)	0.18920 (4)	0.23983 (7)	0.0360 (3)
O1	−0.3592 (9)	0.1363 (3)	0.4798 (4)	0.0476 (12)
O2	−0.0640 (9)	0.2045 (3)	0.3690 (4)	0.0450 (12)
O3	−0.0217 (8)	0.2219 (3)	0.1054 (5)	0.0436 (11)
O4	0.4878 (9)	0.1503 (3)	0.0551 (5)	0.0536 (13)
C1	−0.2190 (13)	−0.0229 (4)	0.3452 (6)	0.038 (2)
C2	−0.1346 (14)	−0.0909 (4)	0.2711 (7)	0.047 (2)
C3	0.0567 (14)	−0.0780 (4)	0.1832 (7)	0.045 (2)
C4	0.1683 (13)	0.0015 (4)	0.1665 (6)	0.039 (2)
C5	0.0789 (12)	0.0699 (4)	0.2407 (6)	0.0335 (14)
C6	−0.1106 (11)	0.0574 (4)	0.3278 (6)	0.0305 (14)
C7	−0.1918 (12)	0.1345 (4)	0.4002 (6)	0.0334 (14)
H31	0.0299	0.2578	0.0418	0.050
H42	0.4262	0.1943	−0.0027	0.050
H41	0.6344	0.1844	0.0629	0.050

Table 2. *Selected geometric parameters* (Å, °)

As—O3	1.763 (5)	C1—C6	1.385 (8)
As—O2	1.925 (4)	C2—C3	1.384 (10)
As—C5	1.945 (6)	C3—C4	1.381 (9)
As···O4	2.560 (5)	C4—C5	1.396 (9)
O1—C7	1.217 (7)	C5—C6	1.371 (8)
O2—C7	1.324 (7)	C6—C7	1.479 (8)
C1—C2	1.382 (9)		
O3—As—O2	93.4 (2)	C3—C4—C5	117.6 (6)
O3—As—C5	96.2 (2)	C6—C5—C4	120.5 (6)
O2—As—C5	84.2 (2)	C6—C5—As	111.4 (4)
O3—As···O4	83.5 (2)	C4—C5—As	128.1 (5)
O2—As···O4	171.5 (2)	C5—C6—C1	121.5 (6)
C5—As···O4	88.3 (2)	C5—C6—C7	115.8 (5)
C7—O2—As	115.6 (4)	C1—C6—C7	122.7 (5)
C2—C1—C6	118.6 (6)	O1—C7—O2	121.7 (6)
C3—C2—C1	119.8 (6)	O1—C7—C6	125.4 (6)
C2—C3—C4	122.0 (6)	O2—C7—C6	113.0 (5)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	*D*—H	*D*···*A*	*D*—H···*A*
O4—H42···O2^{i}	0.941 (5)	2.94 (1)	158 (1)
O3—H31···O1^{i}	0.903 (4)	2.70 (1)	153 (1)
O4—H41···O3^{ii}	0.927 (5)	2.79 (1)	161.5 (1)

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $1 + x, y, z$.

H atoms attached to the water molecule and the hydroxyl group were located by difference Fourier synthesis and were included in the refinement with constraints (keeping the H atoms at angular positions found from difference Fourier maps). All other H atoms were located by geometric considerations and refined as riding on their carrier atoms.

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*95 (Sheldrick, 1995).

MSH thanks the Guru Nanak Dev University for providing a grant for the purchase of a computer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DE1033). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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