

C(8)—O(1)—C(7)—C(6)	-166.6	O(4)—P(1)—C(9)—N(1)	55.3
C(7)—O(1)—C(8)—O(2)	3.1	O(4)—P(1)—C(9)—C(10)	-179.8
C(7)—O(1)—C(8)—N(1)	-179.1	O(5)—P(1)—C(9)—N(1)	167.7
C(9)—N(1)—C(8)—O(1)	-179.2	O(5)—P(1)—C(9)—C(10)	-67.4
C(9)—N(1)—C(8)—O(2)	-1.4	C(8)—N(1)—C(9)—P(1)	-92.3
O(3)—P(1)—C(9)—N(1)	-67.4	C(8)—N(1)—C(9)—C(10)	143.2
O(3)—P(1)—C(9)—C(10)	57.5		

D—H...A	H...A	D—H...A
N(1)—H(1A)...O(2 ⁱ)	1.963	155.8
O(4)—H(4A)...O(3 ⁱⁱ)	2.253	111.5
O(5)—H(5A)...O(3 ⁱⁱⁱ)	1.812	149.3

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

The crystal was mounted along the largest dimension and data were collected with a diffractometer equipped with a copper rotating anode and a highly oriented graphite monochromator using a constant scan speed of 8° min^{-1} in ω . Weak reflections [$I < 5\sigma(I)$] were rescanned a maximum of four times and the counts accumulated to assure good counting statistics. The data were corrected for Lorentz and polarization effects.

The systematic absences ($0k0, k = 2n + 1$) indicated a choice between the $P2_1$ and $P2_1/m$ space groups. Since the molecule is chiral, the former space group was chosen. All non-H atoms were refined anisotropically by the full-matrix least-squares method. H atoms were included in ideal positions with a fixed isotropic $U = 0.08 \text{ \AA}^2$. The final difference map was devoid of significant features.

All calculations were performed on a Silicon Graphics Personal Iris 4D/35 IBM-compatible PC. TEXSAN (Molecular Structure Corporation, 1990) was used for data reduction, SHELXS86 (Sheldrick, 1990a) for structure solution and SHELXTL (Sheldrick, 1990b) for structure refinement.

We are grateful to Professor Richard E. Marsh at California Institute of Technology, USA, for his helpful comments on the manuscript.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MD1002). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Redetermination of 4-Hydroxy-3-nitrobenzenearsonic Acid

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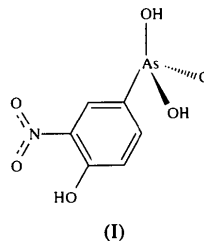
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Abstract

The structure of the title compound, C₆H₆AsNO₆, has been redetermined to provide a more accurate molecular model. The molecule contains a pentavalent As atom coordinated in an approximately tetrahedral configuration to three O atoms and a benzene ring C atom. The molecules are linked by a network of hydrogen bonds between the O atoms of the arsonic group, around centres of inversion.

Comment

Organo-arsenic compounds have attracted interest because of their possible biomedical uses (Dhubhghaill & Sadler, 1991) and numerous structural studies have been carried out by obsolete photographic methods. One such example is the title compound, (I) (Chatterjee & Sen Gupta, 1977), where oscillation and Weissenberg photographs were taken along three crystallographic axes with Cu $K\alpha$ radiation, and the intensities were measured visually using the multiple-film technique. The structure was refined to $R = 0.12$ for 1271 observed reflections and no absorption correction was applied. This redetermination, using modern diffraction apparatus and computational methods, is in good agreement with the model determined by Chatterjee & Sen Gupta (1977) but improves the accuracy quite significantly. For example, the R factor is reduced to 0.058 and uncertainties in bond lengths and angles are reduced by a factor of two or more.



H atoms on the benzene ring were generated in their most logical positions and included in the structure-factor calculations but not refined. Attempts were made to locate the H atoms associated with the arsonic and

hydroxy groups by inspection of difference Fourier maps, but to no avail. Given the uncertainty with which such atoms could be placed on geometrical criteria alone, we decided not to include these H atoms in the model. There were no reflections suitable for an experimental absorption correction and accordingly empirical corrections calculated using *DIFABS* (Walker & Stuart, 1983) were applied. Although this method is not preferable to an experimentally derived correction, it has been useful in this analysis, resulting in a reduction in the conventional *R* value from *ca* 0.12 to 0.058. The Durbin–Watson *d* statistic (Flack & Vincent, 1980) of value 2.1 suggests that the absorption correction had been correctly applied.

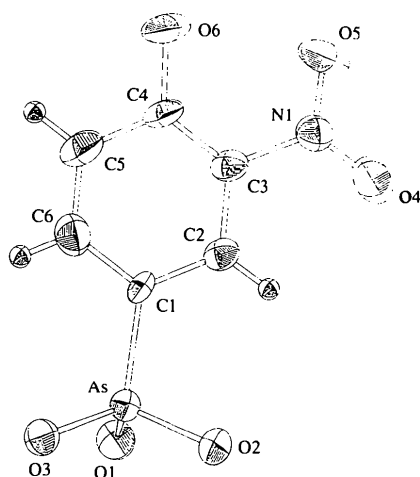


Fig. 1. ORTEP (Johnson, 1976) diagram of the title compound showing the numbering scheme used. Ellipsoids are represented at the 50% probability level.

The pentavalent As atom displays an almost tetrahedral bonding configuration. A survey of As—O intramolecular distances in the Cambridge Structural Database (Allen, Davies, Galloy, Johnson, Kennard, Mitchell, Mitchell, Smith & Watson, 1991) indicates that the mean As—O bond length is 1.77 Å and the mean As=O distance is 1.67 Å. We would like to point out that there are a number of poorly characterized structures in the database used to provide these mean bond lengths. The presence of one double bond of length 1.654 Å and two single As—O bonds of lengths 1.689 and 1.705 Å is inferred.

Molecules are linked together around the inversion centres by intermolecular hydrogen bonds between the O atoms of the arsonic groups. There is a hydrogen bond between O1 (of molecule 1) and O3 (at $-x, -y, 1 - z$) of length 2.614 (5) Å and one between O1 (molecule 1) and O2 (at $-x, -y, -z$) of length 2.623 (5) Å.

Experimental

The title compound was purchased from Aldrich, and crystallized from a 1:1 water:ethanol mixture.

Crystal data

$C_6H_6AsNO_6$	Cu $K\alpha$ radiation
$M_r = 263.04$	$\lambda = 1.54184 \text{ \AA}$
Triclinic	Cell parameters from 20 reflections
$P\bar{1}$	$\theta = 13\text{--}23^\circ$
$a = 6.658 (1) \text{ \AA}$	$\mu = 5.566 \text{ mm}^{-1}$
$b = 11.528 (2) \text{ \AA}$	$T = 295 (1) \text{ K}$
$c = 5.695 (2) \text{ \AA}$	Plate
$\alpha = 101.47 (3)^\circ$	$0.75 \times 0.45 \times 0.02 \text{ mm}$
$\beta = 95.59 (2)^\circ$	Colourless
$\gamma = 92.24 (2)^\circ$	
$V = 425.6 (3) \text{ \AA}^3$	
$Z = 2$	
$D_x = 2.052 \text{ Mg m}^{-3}$	

Data collection

Rigaku AFC-5 diffractometer	1020 observed reflections
$\omega/2\theta$ scans	$[I > 3\sigma(I)]$
Absorption correction: refined from ΔF (<i>DIFABS</i> ; Walker & Stuart, 1983) (see <i>Comment</i>)	$R_{\text{int}} = 0.032$
1129 measured reflections	$\theta_{\text{max}} = 60.1^\circ$
1034 independent reflections	$h = 0 \rightarrow 7$
	$k = -13 \rightarrow 13$
	$l = -6 \rightarrow 6$
	3 standard reflections monitored every 150 reflections
	intensity decay: 6%

Refinement

Refinement on F	$w = 4F_o^2/\sigma^2(F_o^2)$
$R = 0.058$	$(\Delta/\sigma)_{\text{max}} = 0.01$
$wR = 0.082$	$\Delta\rho_{\text{max}} = 1.29 \text{ e \AA}^{-3}$
$S = 1.06$	$\Delta\rho_{\text{min}} = -0.77 \text{ e \AA}^{-3}$
1020 reflections	Extinction correction: none
127 parameters	Atomic scattering factors from Cromer & Waber (1974)
H-atom parameters not refined	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
As	-0.20129 (6)	0.07176 (4)	0.24071 (9)	2.07 (4)
O1	0.0449 (5)	0.0968 (3)	0.3169 (7)	2.6 (1)
O2	-0.2677 (5)	0.0509 (4)	-0.0593 (7)	3.2 (2)
O3	-0.2800 (5)	-0.0574 (3)	0.315 (1)	2.9 (1)
O4	-0.8570 (6)	0.2927 (5)	0.019 (1)	4.4 (2)
O5	-0.9340 (7)	0.4093 (5)	0.339 (1)	5.6 (2)
O6	-0.6844 (7)	0.4632 (4)	0.7235 (9)	4.1 (2)
N1	-0.8206 (7)	0.3391 (5)	0.228 (1)	3.3 (2)
C1	-0.3520 (7)	0.1984 (5)	0.377 (1)	1.9 (2)
C2	-0.5254 (7)	0.2253 (4)	0.250 (1)	2.3 (2)
C3	-0.6391 (7)	0.3151 (5)	0.368 (1)	2.6 (2)
C4	-0.5827 (8)	0.3755 (5)	0.599 (1)	2.6 (2)
C5	-0.402 (1)	0.3500 (5)	0.719 (1)	3.6 (2)
C6	-0.2891 (8)	0.2611 (6)	0.606 (1)	3.3 (2)

Table 2. Selected geometric parameters (Å, °)

As—O1	1.654 (3)	N1—C3	1.448 (7)
As—O2	1.689 (4)	C1—C2	1.382 (7)
As—O3	1.705 (3)	C1—C6	1.379 (9)
As—C1	1.885 (5)	C2—C3	1.407 (8)
O4—N1	1.201 (7)	C3—C4	1.369 (9)
O5—N1	1.249 (7)	C4—C5	1.398 (8)
O6—C4	1.360 (7)	C3—C4	1.369 (8)
O1—As—O2	113.3 (2)	C2—C1—C6	120.9 (5)
O1—As—O3	109.6 (2)	C1—C2—C3	117.4 (5)
O1—As—C1	113.1 (2)	N1—C3—C2	115.3 (6)
O2—As—O3	104.5 (2)	N1—C3—C4	122.2 (5)
O2—As—C1	104.9 (2)	C2—C3—C4	122.5 (5)
O3—As—C1	111.1 (2)	O6—C4—C3	125.7 (5)
O4—N1—O5	123.3 (5)	O6—C4—C5	115.3 (6)
O4—N1—C3	120.8 (5)	C3—C4—C5	118.9 (5)
O5—N1—C3	115.9 (6)	C4—C5—C6	119.3 (6)
As—C1—C2	120.1 (4)	C1—C6—C5	121.0 (5)
As—C1—C6	119.0 (3)		

Anomalous-dispersion effects were included in F_c (Ibers & Hamilton, 1964).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992); structure solution: *TEXSAN*; structure refinement: *DIRDIF* (Beurskens, 1984), *MITHRIL* (Gilmore, 1984); molecular graphics: *ORTEPII* (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1011). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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N-(2-Hydroxyphenyl)salicylaldimine

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Abstract

The title compound, 2-(salicylideneamino)phenol, C₁₃H₁₁NO₂, a potential tridentate ligand, has two crystallographically independent molecules in the asymmetric unit, one of which is disordered. Intramolecular hydrogen bonds occur between the pairs of atoms O(16) and N(8) [2.625 (7) Å], and O(1) and O(16) [3.571 (7) Å], the H atoms essentially being bonded to the O atoms.

Comment

Schiff base compounds have been used extensively as ligands in the field of coordination chemistry. Among these bases, salicylaldimines are of interest since intramolecular hydrogen bonding between O and N atoms plays an important role in the formation of metal complexes. Some analytical data are available on the O—H...N hydrogen-bond strength of 2-hydroxyaldimines (Freedman, 1961), but the situation for 2,2'-dihydroxyaldimines has not been explained. Recently, the hydrogen bonding in various Schiff bases was investigated by a potentiometric method (Gündüz, Gündüz, Kilic,