

N8—H8D···O4	0.82 (7)	2.09 (5)	2.622 (4)	123 (6)
N9—H9A···O8 ^{iv}	0.84 (4)	2.36 (4)	3.034 (4)	138 (4)
N9—H9A···N6	0.84 (4)	2.64 (6)	3.236 (6)	129 (4)
N9—H9B···O3	0.87 (5)	2.20 (5)	3.014 (4)	155 (4)
N9—H9C···O8	0.99 (7)	2.01 (7)	2.897 (7)	147 (5)
O7—H7E···N1 ⁱⁱ	0.79 (5)	2.39 (4)	3.072 (4)	146 (4)
O7—H7D···O6 ^v	0.79 (4)	1.96 (4)	2.735 (3)	165 (4)
O8—H8F···O2	0.73 (7)	2.29 (7)	3.012 (4)	176 (7)

Symmetry codes: (i) $x - 1, y, z$; (ii) $x, y - 1, z$; (iii) $x - 1, 1 + y, z$; (iv) $-x, 1 - y, -z$; (v) $1 - x, -y, 1 - z$.

The structure was solved by Patterson and Fourier methods. Non-H atoms were refined anisotropically by full-matrix least-squares techniques. All H atoms were located from difference Fourier maps and refined isotropically.

Data collection: *CAD-4-Express Software* (Enraf–Nonius, 1994). Cell refinement: *CRYSDA* in *DIRDIF* (Beurskens *et al.* 1992). Data reduction: *REFLEX* (local program). Program(s) used to solve structure: *DIRDIF*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Geometrical calculations: *PARST* (Nardelli, 1983). Molecular graphics: *EUCLID* (Spek, 1982). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1110). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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p-Arsanilic Acid, a Redetermination

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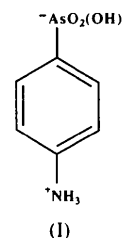
(Received 9 February 1995; accepted 7 December 1995)

Abstract

The title compound, *p*-arsanilic acid, C₆H₈AsNO₃, contains an As atom tetrahedrally coordinated to three O atoms and a C atom of the substituted benzene ring. The molecules are linked by an array of hydrogen bonds arising from three separate interactions formed between N and O atoms and one involving two O atoms. The molecule is in the zwitterionic form (*i.e.* *p*-ammoniophenylarsonate).

Comment

Interest in the structure of arsenicals has in part been stimulated by their biomedical applications. For example, some are still used against trypanosomal infection despite their toxicity (Dhubhghail & Sadler, 1991; Zwegarth & Kaminsky, 1990). Shimada (1961) previously characterized the structure of *p*-arsanilic acid, (I), using Weissenberg and oscillation photography and visual estimation of intensities. The original publication omitted details pertaining to the precision of the structure. For example, no standard deviations are given. Our analysis improves the precision and fully documents the structure. Shimada (1961) concluded from his analysis that the sample is a mono-acid; this proposal is reassessed.



The As—O bond distances indicate one As—O bond of length 1.737 (8) Å and two As=O bonds of length 1.656 (6) and 1.669 (5) Å. As—O bond distances have been assigned in the *ortho*-acid structure by Chatterjee & Gupta (1977); one As=O bond of length 1.64 Å and two As—O single bonds of length 1.73 Å were observed. For comparative purposes, an analysis of bond lengths observed in the compounds stored in the Cambridge Structural Database (Allen *et al.*,

1991) was carried out. The mean As—O bond length, based on 462 examples, is 1.77 Å, with a mean standard deviation of 0.004 Å. The mean As=O length, derived from 87 examples, is 1.67 Å, with a mean standard deviation of 0.003 Å.

A comparison of the C—N intramolecular distance with examples in the Cambridge Structural Database was made: the mean C—NH₂ length is 1.37 Å (427 values, mean standard deviation 0.001 Å), the mean C—NH₃⁺ is 1.47 Å (92 examples, mean standard deviation of 0.001 Å), and, in the present study, C4—N is 1.48 (1) Å. This indicates that the molecule contains an NH₃⁺ group, is monobasic and that the crystal structure is of the zwitterionic form, confirming the results of Shimada (1961).

The molecules are linked together by a network of three hydrogen bonds formed by the NH₃⁺ moiety with arsonic atoms O1 and O2 of symmetry-related molecules and one involving the hydroxy O3 atom and the arsonic O2 atom of a symmetry-related molecule. The relevant atoms and distances are: for the two N···O1 contacts 2.686 (8) and 2.712 (9) Å, for N···O2 2.678 (9) Å, and for O3···O2 2.608 (8) Å. Although the distances differ from those of the previous determination (Shimada, 1961), the assignment of the hydrogen-bonding network is the same.

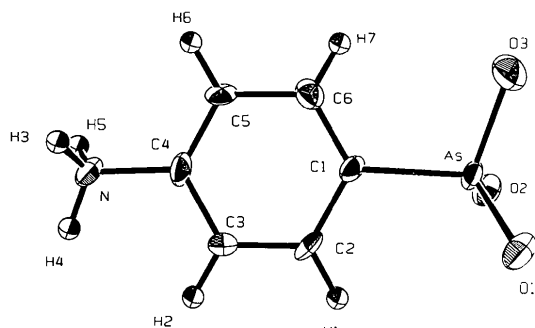


Fig. 1. ORTEP (Johnson, 1976) drawing of *p*-arsanic acid showing the atom-numbering scheme. Ellipsoids are shown at the 50% probability level for non-H atoms.

Experimental

A commercial sample of the title compound was purchased from Aldrich and crystallized from water/methanol.

Crystal data

C₆H₈AsNO₃

M_r = 217.06

Monoclinic

*P*2₁

a = 7.241 (2) Å

b = 6.214 (1) Å

c = 8.643 (1) Å

β = 101.19 (1)°

Cu Kα radiation

λ = 1.54178 Å

Cell parameters from 20 reflections

θ = 21.03–29.05°

μ = 5.75 mm⁻¹

T = 295 (1) K

Plate

V = 381.5 (1) Å³

Z = 2

D_x = 1.889 Mg m⁻³

D_m not measured

0.45 × 0.35 × 0.1 mm

Colourless

Data collection

Rigaku AFC-5R diffractometer

ω/2θ scans

Absorption correction:

refined from Δ*F*

(*DIFABS*; Walker &

Stuart, 1983)

T_{min} = 0.31, *T_{max}* = 0.57

1014 measured reflections

543 independent reflections

537 observed reflections

[*I* > 3σ(*I*)]

R_{int} = 0.065

θ_{max} = 60°

h = 0 → 8

k = -7 → 7

l = -10 → 10

3 standard reflections

monitored every 150

reflections

intensity decay: no

significant variation

Refinement

Refinement on *F*

R = 0.044

wR = 0.055

S = 1.04

537 reflections

99 parameters

H-atom parameters not

refined

w = 1/(*a* + |*F_o*| + *c*|*F_o*|²),

a = 2*F_{min}*, *c* = 2/*F_{max}*

(Δσ)_{max} = 0.02

Δρ_{max} = 0.67 e Å⁻³

Δρ_{min} = -0.66 e Å⁻³

Extinction correction: none

Atomic scattering factors

from Cromer & Waber

(1974)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i>
As	0.16284 (9)	0.0000	0.18292 (6)	1.64 (4)
O1	0.3398 (8)	-0.0623 (8)	0.0953 (5)	2.3 (2)
O2	-0.0454 (8)	-0.0965 (9)	0.0926 (6)	2.2 (2)
O3	0.1476 (9)	0.2778 (13)	0.1994 (7)	3.2 (4)
N	0.3291 (10)	-0.3452 (12)	0.8588 (9)	1.8 (2)
C1	0.2128 (11)	-0.0951 (12)	0.3967 (9)	1.5 (3)
C2	0.2887 (13)	-0.3006 (14)	0.4248 (9)	2.3 (4)
C3	0.3238 (10)	-0.3785 (12)	0.5774 (8)	2.0 (3)
C4	0.2917 (13)	-0.2525 (13)	0.6981 (8)	2.0 (3)
C5	0.2280 (15)	-0.0479 (10)	0.6754 (8)	1.7 (3)
C6	0.1808 (12)	0.0307 (12)	0.1591 (8)	2.0 (3)

Table 2. Selected geometric parameters (Å, °)

As—O1	1.656 (6)	C1—C6	1.371 (11)
As—O2	1.669 (5)	C2—C3	1.381 (11)
As—O3	1.737 (8)	C3—C4	1.360 (11)
As—C1	1.907 (7)	C4—C5	1.354 (12)
N—C4	1.479 (10)	C5—C6	1.415 (10)
C1—C2	1.393 (12)		
O1—As—O2	114.3 (3)	C2—C1—C6	120.6 (7)
O1—As—O3	109.7 (3)	C1—C2—C3	118.8 (6)
O1—As—C1	110.7 (3)	C2—C3—C4	120.2 (7)
O2—As—O3	109.2 (3)	N—C4—C3	118.0 (7)
O2—As—C1	109.0 (3)	N—C4—C5	119.8 (7)
O3—As—C1	103.4 (3)	C3—C4—C5	122.2 (7)
As—C1—C2	116.6 (5)	C4—C5—C6	118.4 (7)
As—C1—C6	122.8 (6)	C1—C6—C5	119.6 (7)

The As atom was located from a Patterson synthesis and the structure completed by direct methods (*MITHRIL*; Gilmore 1984). H atoms could not be located in the difference density

map; seven were generated on the basis of geometrical considerations and their parameters not refined. The H atom attached to O3 was not located. The Durbin-Watson d statistic (Flack & Vincent, 1980) of value 2.07 suggests a suitable molecular model has been attained and that there are no serious systematic errors in the data. Anomalous-dispersion effects were included in F_c (Ibers & Hamilton, 1964). Refinement of the opposite absolute configuration gave $R = 0.065$. The weighting scheme is that of Cruickshank, Pilling, Bujosa, Lovell & Trutter (1961).

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988a). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1988b). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984); *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. 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: CF1008). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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