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3-Nitro-4-hydroxyphenylarsonic Acid

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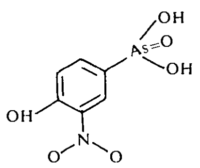
Abstract. $C_6H_6O_6NAs$, triclinic, $P\bar{1}$, $a = 5{\cdot}78\ (2)$, $b = 8{\cdot}42\ (2)$, $c = 11{\cdot}93\ (2)$ Å, $\alpha = 81{\cdot}6\ (2)$, $\beta = 107{\cdot}1\ (2)$, $\gamma = 127{\cdot}9\ (2)^\circ$, $V = 437{\cdot}1$ Å^3, FW 263·02, $Z = 2$, $D_m = 2{\cdot}02$, $D_x = 2{\cdot}00$ g cm^{-3}, μ(Cu $K\alpha$) = 59·5 cm^{-1}. The structure was determined by the heavy-atom method and refined by least squares to $R = 0{\cdot}12$ for 1271 observed reflexions measured from equi-inclination Weissenberg photographs. The As is tetrahedrally connected to C and three O atoms, with the average angle around it being 109·6°. The molecules are linked along **a** through O···O hydrogen bonds between the O atoms of the arsonic acid group around the inversion centre. An intramolecular hydrogen bond occurs between the hydroxyl and one O of the nitro group, O···O = 2·64 Å.

Introduction. Crystals of the title acid (I) were obtained from a mixture of water and alcohol by slow evaporation at room temperature. The cell parameters were derived from oscillation and Weissenberg photographs taken along three crystallographic axes with Cu $K\alpha$ radiation. The chosen unit cell may, however, be reduced (Azaroff & Buerger, 1958) by the transformation matrix $(1\ 0\ 0/-1\ -1\ 0/-1\ 0\ -1)$ to give the following parameters: $a = 5{\cdot}78$, $b = 6{\cdot}67$, $c = 11{\cdot}63$ Å, $\alpha = 91{\cdot}6$, $\beta = 101{\cdot}3$, $\gamma = 95{\cdot}2^\circ$, $V = 436{\cdot}5$ Å^3. No symmetry, except that due to Friedel's law, nor any systematic absences were observed, and the space group was confirmed as $P\bar{1}$ from the $N(z)$ statistical test (Chatterjee & Sen Gupta, 1975).



(I)

Multiple-film equi-inclination Weissenberg photographs for layers $0kl$–$4kl$ and $h0l$–$h2l$ were taken in two different ranges of oscillation (180° apart from each other) to collect unique data over the whole reciprocal space. The intensities of 1271 observed independent reflexions were estimated visually, and corrected for spot size (Phillips, 1954, 1956), Lorentz and polarization factors, but not corrected for absorption (the crystal dimensions were 0·8, 0·7, 0·2 mm). The a-axis data were then placed on the same relative scale by the cross-layer correlation method, and the overall scale and temperature factors were then evaluated by Wilson's (1942) method.

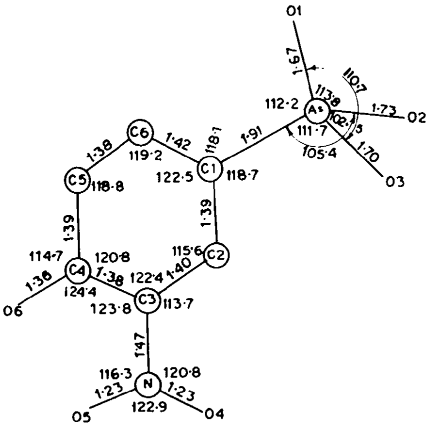


Fig. 1. A schematic diagram of the molecule showing the bond lengths (Å) and angles (°). The e.s.d.'s are 0·01–0·03 Å for bond lengths and 0·7–2·0° for angles.

Table 1. *Positional parameters of non-hydrogen atoms*

The parameters are $\times 10^3$, except As $\times 10^4$. The e.s.d.'s of the parameters appear in parentheses.

	x	y	z
As	1298 (4)	7991 (2)	718 (1)
O(1)	327 (3)	1047 (2)	96 (1)
O(2)	341 (3)	730 (2)	50 (1)
O(3)	−148 (3)	718 (2)	−57 (1)
O(4)	−81 (4)	144 (2)	293 (1)
O(5)	−361 (5)	64 (2)	409 (1)
O(6)	−441 (3)	318 (2)	463 (1)
N	−209 (4)	179 (2)	341 (1)
C(1)	−31 (3)	647 (2)	200 (1)
C(2)	−53 (4)	472 (2)	226 (1)
C(3)	−189 (4)	363 (2)	317 (1)
C(4)	−305 (4)	420 (3)	375 (1)
C(5)	−277 (5)	597 (3)	348 (1)
C(6)	−144 (4)	711 (3)	259 (1)

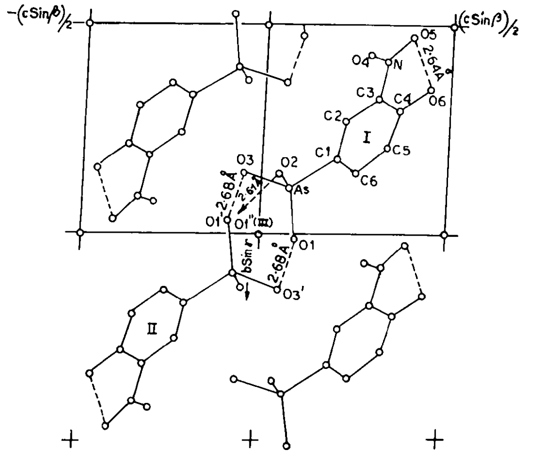


Fig. 2. A projection of the unit-cell contents along **a**, showing the molecular packing and hydrogen bonds.

The position of As was derived from a Patterson synthesis, then the 13 non-hydrogen atoms were located from the first As-phased Fourier synthesis. Three cycles of isotropic refinement by full-matrix least squares with the program *MAMIE* (Vickery, Bright & Mallinson, 1971) reduced R to 0·15. Finally, anisotropic refinement by block-diagonal least squares reduced R to 0·122.* The quantity minimized was $\Sigma w(F_o - F_c)^2$ with $w = 1/(A + B|F_o| + C|F_o|^2)$ (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961), where $A = 3{\cdot}7279$, $B = 0{\cdot}5365$ and $C = 0{\cdot}0362$. The 102 reflexion was excluded from the refinement since it appeared to suffer from extinction. No attempt was made to locate the H atoms. The final positional parameters and their estimated standard deviations are listed in Table 1.

Discussion. The bond lengths and angles are presented in Fig. 1, and the molecular packing with the proposed hydrogen-bonding scheme is illustrated in Fig. 2. The As atom is covalently linked to three O atoms and C(1) of the benzene ring. The disposition of bonds around As is tetrahedral with the average interbond angle at As being 109·4°. As—C is 1·91 Å and the average As—O is 1·70 Å. The C—C lengths of the benzene ring are 1·38–1·42 Å, mean 1·39 Å. The benzene ring is planar, as described in Table 2, with the N and O(6) substituents almost in the plane of the ring. The tetrahedral disposition of the bonds around As and the bond lengths in this structure are in good agreement with the corresponding observations in phenylarsonic acid and its *m*- and *p*-amino derivatives (Shimada, 1959, 1960, 1961, 1962), the *o*-amino derivative of phenylarsonic acid (Chatterjee & Sen Gupta, 1977), and also with the similar findings of Trotter & Zobel (1965) on the stereochemistry of As compounds. The torsion angles of the AsO_3 configuration and of NO_2 relative to the benzene ring are given in the Newman projections in Fig. 3.

3-Nitro-4-hydroxyphenylarsonic acid has three H atoms available for bonding, two from the arsonic group and one from the hydroxyl group. Since the H atoms have not been located, the proposed hydrogen-bonding scheme has been based on the inter- and intramolecular distances. Fig. 2 shows that O(3) of molecule I at (x,y,z) has a close neighbour, O(1′) of

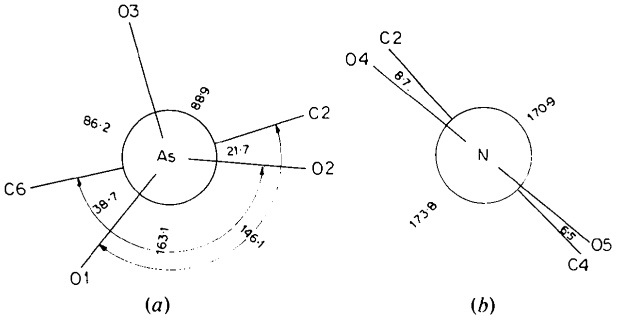


Fig. 3. Newman projections along: (*a*) As—C(1), and (*b*) N—C(3) showing the torsion angles (°) for the AsO_3 and NO_2 groups.

Table 2. *Deviations* (Å) *from the least-squares plane through the phenyl ring*

The plane referred to an orthogonal set of axes is $-0{\cdot}5486X - 0{\cdot}4959Y - 0{\cdot}6730Z = -1{\cdot}2885$, where **X** is along **a**, **Y** in the *ab* plane and **Z** along **c***; $\chi^2 = 1{\cdot}09$. Asterisks identify atoms not included in the plane calculation.

C(1)	−0·003	C(4)	0·012	*As	0·122
C(2)	0·006	C(5)	−0·009	*N	0·006
C(3)	−0·010	C(6)	0·004	*O(6)	0·004

Table 3. *Intermolecular distances below* 3·4 Å

Hydrogen bonds are marked with an asterisk. Superscripts refer to the equivalent positions:

(i)	$1+x, 1+y, z$	(iv)	$-x, 2-y, -z$
(ii)	$1-x, 2-y, -z$	(v)	$1+x, y, z$
(iii)	$-x, 1-y, -z$	(vi)	$-1-x, -y, 1-z$.

$O(1)\cdots O(4^{i})$	3·20	$O(2)\cdots C(6^{v})$	3·35
$O(1)\cdots N^{i}$	3·09	$O(3)\cdots O(1^{iv})$	2·68*
$O(1)\cdots C(2^{i})$	3·26	$O(3)\cdots O(4^{iii})$	3·23
$O(1)\cdots C(3^{i})$	3·22	$O(4)\cdots O(6^{v})$	3·12
$O(2)\cdots O(1^{ii})$	2·61*	$O(5)\cdots O(5^{vi})$	2·78
$O(2)\cdots O(3^{iii})$	3·21	$O(5)\cdots O(6^{vi})$	3·00
$O(2)\cdots C(2^{iii})$	3·38		

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32852 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

molecule II at ($-x$, $2-y$, $-z$), at a distance of 2·68 Å, As–O(3)···O(1′) = 108·9°. Also, O(2) of molecule I has a close neighbour, O(1″) of molecule III at ($1-x$, $2-y$, $-z$) which overlaps in this projection with molecule II, at a distance of 2·61 Å, As–O(2)···O(1″) = 114·0°. These O···O hydrogen bonds link the molecules to form infinite chains along **a**. There is also a possible O(5)···O(6) intramolecular hydrogen bond of length 2·64 Å. All the other intermolecular distances correspond to normal van der Waals interactions, as shown by the list in Table 3. The type of hydrogen bonding observed in this structure is very similar to those observed for phenylarsonic acid (Shimada, 1959) and its *o*-amino derivative (Chatterjee & Sen Gupta, 1977). In the present case, however, only O···O hydrogen bonds are formed.

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Disilber-sulfamid

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Abstract. $SO_2(NHAg)_2$, monoclinic, $P2_1/c$ (No. 14), $a = 7{\cdot}661\ (1)$, $b = 5{\cdot}719\ (1)$, $c = 10{\cdot}464\ (1)$ Å, $\beta = 93{\cdot}89\ (2)°$, $V = 457{\cdot}4$ Å^3, $Z = 4$, $D_m = 4{\cdot}53$, $D_x = 4{\cdot}49$ g cm^{-3}. Single crystals have been prepared by the reaction of $AgNO_3$ with sulphamide in aqueous solution after neutralization with NH_3. The compound consists of discrete SO_2N_2 tetrahedra with S as the central atom. Each Ag atom is bonded to two N atoms of different tetrahedra. In this way, double chains parallel to **c** are formed. The double chains are linked by hydrogen bonds.

Einleitung. Die Messung der Intensitäten erfolgte mittels integrierter Weissenbergaufnahmen (Cu $K\alpha$, Mehrfachfilmmethode). Es fanden drei verschiedene prismatische Kristalle mit einem mittleren Durchmesser von 0,08 mm Verwendung, $\mu = 735{,}7$ cm^{-1}. Aus Aufnahmen von 11 Schichtlinien um die Drehrichtungen [001], [100] und [010] erhielten wir 925 unabhängige Reflexe, von denen 164 als nicht beobachtet gewertet wurden. An den photometrisch bestimmten Intensitäten führten wir Korrekturen mit dem Lorentz- und dem Polarisationsfaktor sowie eine Absorptionskorrektur für zylindrische Kristalle durch (*International Tables for X-ray Crystallography*, 1959). Die Streukurven für die Berechnung der Strukturfaktoren entnahmen wir den *International Tables for X-ray Crystallography* (1962). Die von