Table 4. *Bond angles* (°) *around the* W *atom* (∠O—W—O)

For symmetry code see Table 3.

| | O($3^{v}$) | O(4) | O($4^{iii}$) | O(5) | O(6) |
|---|---|---|---|---|---|
| O($3^{iii}$) | 75·1 (0·8) | 83·4 (0·8) | 85·2 (0·7) | 171·0 (1·0) | 86·9 (0·8) |
| O($3^{v}$) | | 148·7 (0·7) | 82·6 (0·8) | 96·8 (1·0) | 105·5 (0·9) |
| O(4) | | | 73·2 (1·0) | 105·6 (1·0) | 95·6 (0·9) |
| O($4^{iii}$) | | | | 97·7 (1·0) | 166·9 (0·9) |
| O(5) | | | | | 91·7 (1·0) |

essentially the same. The topotactic relation to the scheelite type is indicated in Fig. 2, where dotted lines show the scheelite-like unit cell. The following relations exist between the two unit cells: $\mathbf{a}_r = -\mathbf{b}_s + \mathbf{c}_s$, $\mathbf{b}_r = \mathbf{a}_s$, $\mathbf{c}_r = \mathbf{b}_s$ (*r* raspite, *s* scheelite-like).

It is expected from these facts that the irreversible phase transformation (Shaw & Claringbull, 1955) from raspite to stolzite, the scheelite-type modification of $PbWO_4$, may be of displacive character. The displacements of the O atoms are small while those of the cations are relatively large.

Bond lengths and bond angles are listed in Tables 3 and 4 respectively. They were calculated with the program *ORFFE* (Busing, Martin & Levy, 1964). All the calculations for this study were carried out on the FACOM 270-20 of the National Institute for Researches in Inorganic Materials.

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# *o*-Aminophenylarsonic Acid

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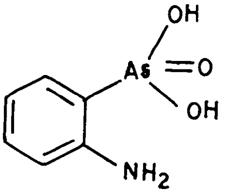
**Abstract.** $C_6H_8O_3NAs$, monoclinic, $P2_1$, $a = 8·44$ (2), $b = 4·93$ (2), $c = 10·33$ (2) Å, $\beta = 110·6$ (2)°; $M_r = 217·04$, $Z = 2$, $D_x = 1·78$, $D_m = 1·79$ g cm$^{-3}$. The structure was determined by the heavy-atom method and refined by least squares to an $R$ of 0·086 for 628 observed reflexions measured from equi-inclination Weissenberg photographs. Molecules are linked together through O—H···O hydrogen bonds around the twofold screw axis. The As atom is tetrahedrally connected to two OH groups, O(2) and C(1) of the benzene ring, the average tetrahedral angle around it being 109° 24′.

**Introduction.** Crystals of *o*-aminophenylarsonic acid (I) suitable for X-ray structural analysis were obtained from a mixture of water and alcohol. Cell constants were determined from oscillation and Weissenberg photographs taken with Cu $K\alpha$ radiation ($\lambda = 1·5418$ Å). The Weissenberg photographs showed systematic absences corresponding to space groups $P2_1$ and

$P2_1/m$ ($0k0$ with $k$ odd); $P2_1$ was later confirmed by the $N(z)$ statistical test (Chatterjee & Sen Gupta, 1976).



(I)

Sets of multiple-film equi-inclination Weissenberg photographs were taken with the crystal rotating about the unique axis *b* (layers *h*0*l* through *h*3*l*). A total of 628 independent reflexions were measured by visual comparison with standard calibrated strips. The intensity values for different layers were corrected for spot size (Phillips, 1954, 1956) and for Lorentz and polarization factors. The unique-axis data were then placed on the same relative scale with the help of a zero-layer Weissenberg photograph about the other axis (*a*) by the cross-layer correlation method. Finally, the absolute scale for different layers and the overall temperature factors were evaluated by Wilson's (1942) method. No absorption corrections were, however, applied for the crystal of approximately cylindrical cross-section (with a diameter of 0·5 to 0·2 mm).

The position of the As atom was derived from the As–As Harker vectors of a three-dimensional Patterson synthesis; this was also confirmed from the two zero-layer Patterson projections about the *b* and *a* axes. The structure factors were calculated for all the reflexions with the coordinates of the As atom only. *R* at this stage was 0·38. A three-dimensional Fourier synthesis was then calculated with the phases based only on the contribution from the As atom. The electron density peaks thus obtained were sufficient to locate all the lighter atoms and subsequently helped to build a model of the structure which appeared to be stereochemically satisfactory. The positional parameters of these atoms were then introduced into a structure factor calculation which led to a conventional *R* of 0·30.

Refinement of the structure was carried out by full-matrix least-squares calculations using the program *MAMIE* of the *X-RAY ARC IBM* 1130 program system (Vickery, Bright & Mallinson, 1971). The function minimized during least-squares refinement was $\Sigma\, w(|F_o| - |F_c|)^2$, where $w$ was initially set as 1. The atomic scattering factors for As, O, N, C and H were obtained from the respective values computed from Hartree–Fock–Slater wave functions (Hanson, Herman, Lea & Skillman, 1964). Four cycles of refinement converged to an *R* of 0·092. Refinement was then continued for three block-diagonal least-squares cycles with anisotropic temperature coefficients and *R* reduced to 0·089. At this stage of refinement a three-dimensional difference Fourier synthesis with $F_c$ values obtained from the refined heavy-atom positions gave the approximate positions of eight H atoms. The H positions were, however, located from considerations of the peaks of the difference synthesis, the accepted stereochemical concepts and the observed change in *R*. The H atoms were then included in a further refinement cycle in which they were held fixed at the calculated positions and assigned isotropic temperature factors equal to those of the atoms to which they were bonded. At this stage, the weighting function $w = 1/(A + B|F_o| + C|F_o|^2)$ (Cruickshank, Pilling, Bijosa, Lovell & Truter, 1961) was introduced, where $A = 1\cdot7032$, $B = 0\cdot0321$ and $C = 0\cdot0039$. Finally, *R* converged to 0·086 for 628 observed reflexions, and 0·100 when 109 unobserved reflexions were included.

The final positional parameters and anisotropic temperature coefficients with their estimated standard deviations for non-H atoms are given in Table 1.

Table 1. *Final positional and anisotropic thermal parameters of non-*H *atoms in o-aminophenylarsonic acid*

The parameters are $\times 10^3$, except for As which is $\times 10^4$. The thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. E.s.d.'s are in parentheses.

| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| As | 2175 (2) | 0* | 1742 (2) | 95 (3) | 253 (14) | 66 (2) | −3 (14) | 21 (2) | −1 (12) |
| O(1) | 133 (2) | −224 (5) | 264 (2) | 18 (3) | 30 (16) | 15 (2) | 1 (5) | 10 (2) | 1 (5) |
| O(2) | 115 (2) | 287 (5) | 159 (2) | 14 (3) | 9 (13) | 10 (2) | 9 (4) | 0 (2) | −3 (4) |
| O(3) | 194 (2) | −135 (5) | 17 (1) | 11 (2) | 58 (15) | 4 (1) | −2 (5) | 0 (1) | −2 (3) |
| N | 483 (2) | 367 (6) | 98 (2) | 11 (3) | 63 (21) | 6 (2) | 0 (6) | 2 (2) | 8 (4) |
| C(1) | 458 (2) | 22 (13) | 270 (2) | 10 (3) | 15 (19) | 8 (2) | 7 (10) | 4 (2) | 8 (8) |
| C(2) | 561 (3) | 186 (7) | 213 (2) | 10 (3) | 27 (17) | 9 (3) | 0 (7) | 6 (2) | −1 (6) |
| C(3) | 735 (3) | 184 (9) | 280 (2) | 11 (4) | 96 (24) | 8 (2) | −1 (9) | 5 (3) | 4 (7) |
| C(4) | 810 (3) | 31 (16) | 390 (2) | 9 (3) | 118 (39) | 7 (2) | 13 (14) | 1 (2) | 3 (12) |
| C(5) | 705 (3) | −152 (7) | 435 (2) | 12 (4) | 27 (18) | 8 (3) | 3 (8) | 0 (3) | −1 (6) |
| C(6) | 533 (2) | −153 (7) | 380 (2) | 9 (3) | 38 (17) | 5 (2) | 8 (7) | 0 (2) | 6 (5) |

* The *y* coordinate of As was fixed to define the origin.

Probable positions and isotropic temperature factors for H atoms are shown in Table 2.*

**Discussion.** The bond lengths and angles for the title compound are shown in Fig. 1, and the molecular packing and hydrogen-bonding scheme when projected onto the plane normal to the *a* axis are illustrated in Fig. 2. The As atom is covalently linked to a group of three O atoms and one C atom of the benzene ring. The disposition of bonds around As is tetrahedral, the average of the angles between the bonds being 109° 24′. The As—C distance is 1·92 and the average of the two As—O bonds is 1·73 whereas the double-bond distance between As and O atoms is 1·64 Å. The average distance between adjacent C atoms in the benzene ring is 1·39, individual values ranging from 1·33 to 1·45 Å. The N—C distance is 1·45 Å. The benzene ring is planar to a good approximation as shown in the mean-plane calculation in Table 3 and, within experimental error, the N atom is found to lie almost on the plane passing through the benzene ring. Deviations of the atoms from the least-squares plane through the phenyl ring are also listed in Table 3. The tetrahedral dispositions of the bonds around As and the interatomic

## Table 2. *Probable hydrogen-atom positions in o-aminophenylarsonic acid*

The H atom is given followed by the atom to which it is bonded (in square brackets), the bond distance in Å, the positional parameters $\times 10^3$ and the isotropic thermal parameters (Å$^2$) used in the least-squares calculations.

| | Bond distance | *x* | *y* | *z* | *B* |
|---|---|---|---|---|---|
| H(1) [O(1)] | 1·21 | 99 | −433 | 199 | 4·1 |
| H(2) [O(3)] | 1·29 | 33 | −133 | −49 | 2·7 |
| H(3) [N] | 1·06 | 566 | 496 | 49 | 3·0 |
| H(4) [N] | 1·18 | 349 | 383 | 66 | 3·0 |
| H(5) [C(3)] | 1·05 | 816 | 333 | 266 | 3·4 |
| H(6) [C(4)] | 0·97 | 933 | 25 | 433 | 3·2 |
| H(7) [C(5)] | 0·98 | 750 | −200 | 533 | 3·3 |
| H(8) [C(6)] | 0·94 | 466 | −200 | 433 | 2·5 |

## Table 3. *Deviations* (Å) *of atoms from the least-squares plane through the phenyl ring*

The equation for the plane is in the form $AX+BY+CZ=D$, where $X$, $Y$ and $Z$ are coordinates (Å) referred to the orthogonal axes *a*, *b* and *c**; *D* (Å) is the distance of the plane from the origin. Daggers indicate atoms not included in the calculation of the plane.

Equation of the least-squares plane through the phenyl ring ($\chi^2=4\cdot2083$): $0\cdot2955X-0\cdot7272Y-0\cdot6195Z=-0\cdot8069$.

| | | | |
|---|---|---|---|
| C(1) | −0·037 | †As | 0·119 |
| C(2) | 0·035 | †O(1) | 0·077 |
| C(3) | 0·003 | †O(2) | −1·058 |
| C(4) | −0·038 | †O(3) | 1·654 |
| C(5) | 0·037 | †N | 0·004 |
| C(6) | 0·000 | | |

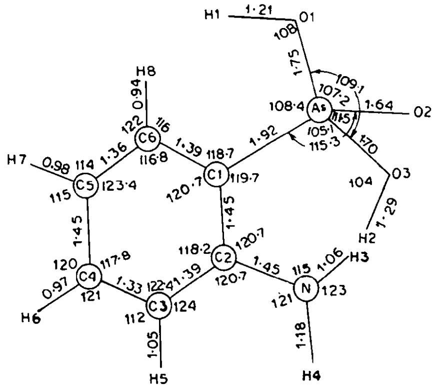


Fig. 1. A schematic diagram of the molecule showing the numbering of the atoms and the bond distances (Å) and angles (°). E.s.d.'s for bond distances between non-H atoms range from 0·01 to 0·05 Å, except for bonds containing C(1) and C(4) for which they vary from 0·05 to 0·06 Å. E.s.d.'s for bond angles are in the range of 0·9 to 2·5°, except for bond angles around C(1) and C(4) where they vary from 2·6 to 3·9°.

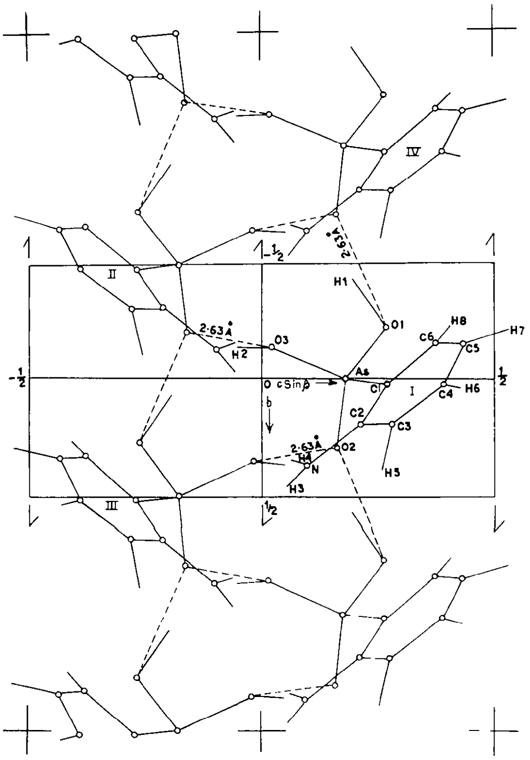


Fig. 2. Molecular packing projected onto the plane normal to the *a* axis. Dashed lines represent hydrogen bonds.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32001 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

distances obtained in this structure are found to be in good agreement with the corresponding observations in phenylarsonic acid and its *m*- and *p*-amino derivatives (Shimada, 1959, 1960, 1961, 1962), and also with the similar findings by Trotter & Zobel (1965) on the stereochemistry of As compounds. The torsional angle of the $-AsO_3$ configuration is, however, defined in the Newman projection along the As—C(1) bond (see Fig. 3).

*o*-Aminophenylarsonic acid has four H atoms available for hydrogen bonding, two from O(1) and O(3) of the arsonic acid group and another two from the N of the *o*-amino group. Fig. 2 shows that O(3) of one molecule (the reference molecule I at $x, y, z$) has a close neighbour O(2) of another molecule (molecule II at $\bar{x}, y-\frac{1}{2}, \bar{z}$) at a distance of 2·63 Å and makes an angle As—O(3)···O(2) of 117·8°. In a similar way atom O(2) of the reference molecule has a close neighbour O(3) of another molecule (molecule III at $\bar{x}, y+\frac{1}{2}, \bar{z}$) at a distance of 2·63 Å and makes an angle As—O(2)···O(3) of 123·7°. Again, O(1) of molecule I has a close neighbour O(2) of molecule IV (the molecule displaced by a unit translation along −**b**) at a distance of 2·63 Å and makes an angle As—O(1)···O(2) of 109·3°. This type of hydrogen bonding between the O atoms of the arsonic acid group links molecules with each other to form endless chains along the screw axis perpendicular to the (010) plane. The N atom has two close neighbours, one O(3) of the same molecule at a distance of 3·35 Å and making an angle C(2)—N···O(3) of 80·2° and another N atom of molecule V at $1+\bar{x}, y+\frac{1}{2}, \bar{z}$ (not shown in Fig. 2 as it overlaps with molecule III in projection) at a distance of 3·27 Å and making an angle C(2)—N···N of 149·2°. Although the bond lengths N—H···O(3) 3·35 and N—H···N 3·27 Å suggest a possible weak intramolecular and intermolecular hydrogen bonding respectively, both the angles C(2)—N···O(3) = 80·2 and C(2)—N···N = 149·2° deviate appreciably from the value for forming normal hydrogen bonds. The intermolecular contacts between non-bonded atoms are found to be of normal van der Waals type with no unusually close approaches other than the 3·48 Å between N of molecule I and C(2) of molecule V.

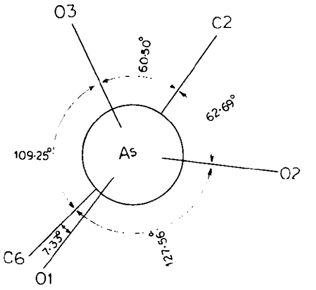

Fig. 3. Newman projection along the As—C(1) bond showing the torsional angles (°) for the $-AsO_3$ configuration relative to the phenyl group.

The type of hydrogen bonding observed here for *o*-aminophenylarsonic acid, however, appears to differ from those types observed in the *m*- and *p*-isomers (Shimada, 1961, 1962). In the latter cases there is one hydrogen bond between O atoms and three hydrogen bonds between O and N atoms in the crystal.

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