

# The Crystal Structure of *p*-Aminobenzenearsonic Acid\*

By Akira SHIMADA

(Received August 6, 1960)

The crystal structure of benzenearsonic acid has recently been reported by the present author<sup>1)</sup> to reveal the molecular configuration of an organoarsenic compound and the hydrogen-bond formation in this crystal. In connection with the above work, the crystal structure of *p*-aminobenzenearsonic acid,  $\text{H}_2\text{N}\cdot\text{C}_6\text{H}_4\text{AsO}(\text{OH})_2$ , was undertaken as a part of a program concerned with the crystal chemistry of organoarsenic compounds.

This study has another interest, since the sodium salt of this acid has always proved of great value in medicine under the name of "Atoxyl".

## Experimental

Suitable crystals for X-ray work were selected from the specimens kindly prepared and supplied by Professor H. Nakata of Konan University. They were colorless, transparent needles with a long dimension in the *b* direction. Oscillation and

Weissenberg photographs were taken with  $\text{Cu } K_\alpha$  radiation, and they showed that the unit cell is monoclinic with the following dimensions:

$a=7.35 \text{ \AA}$ ,  $b=6.35 \text{ \AA}$ ,  $c=8.81 \text{ \AA}$ , and  $\beta=101^\circ$

It was already shown by Gilta<sup>2)</sup> that this crystal belongs to the monoclinic system with the axial ratios,  $a:b:c=1.162276:1:1.393499$ , and the monoclinic angle,  $\beta=101^\circ 20'$ . The axial ratios given above by the morphological method can be compared with, 1.157:1:1.387, the values derived by the X-ray measurement. Two formula units per unit cell results in a calculated density  $1.786 \text{ g. cm}^{-3}$ .

The only extinction rule was found for  $(0k0)$  with *k* odd, which indicates the probable space group  $\text{P2}_1$  with the fact that a symmetry plane is not permissible, and this was confirmed in the course of the structure analysis. All the intensities were estimated visually with a calibrated scale, by making use of the multiple-film technique. The data were recorded from small crystals [cross sections with rectangular dimensions;  $0.18 \times 0.11 \text{ mm.}$  for  $(h0l)$ , and  $0.09 \times 0.21 \text{ mm.}$  for  $(0kl)$ ], and

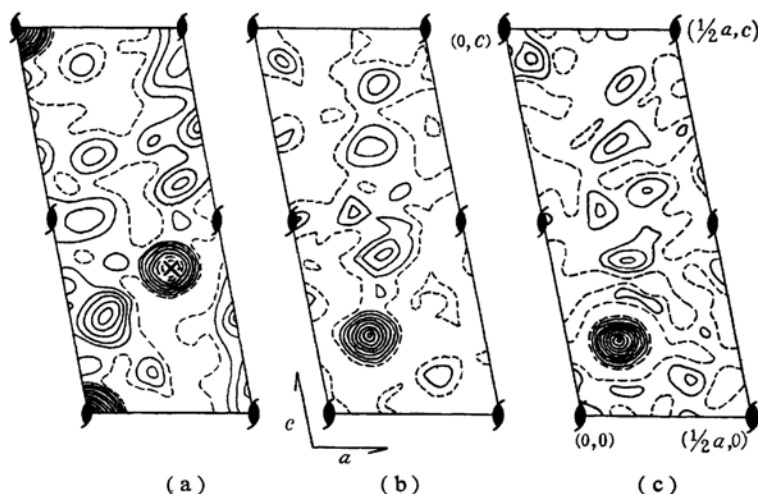


Fig. 1. (a) The Patterson projection,  $P(UW)$ , along the *b* axis, the rotation peak due to arsenic atoms being marked by a cross. Contours at arbitrary scale. (b) The minimum function,  $M_2(XZ)$ , derived from the rotation peak in Fig. 1a. (c) The electron-density projection,  $\rho_1(XZ)$ , for comparison with  $M_2(XZ)$  in Fig. 1b. Contours at arbitrary scale.

\* The major part of this paper was read at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960.

1) A. Shimada, *This Bulletin*, 32, 309 (1959); A. Shimada, *ibid.*, 33, 301 (1960).

2) G. Gilta, *Bull. soc. chim. Belges*, 32, 19 (1923).

\*\* The density was measured to be  $1.9571 \text{ g. cm}^{-3}$  by Lorenz and Schmidt (*Z. anorg. u. allgem. Chem.* 112, 269 (1920)), and the author obtained the value of  $1.85 \text{ g. cm}^{-3}$  by floatation in bromoform and carbon tetrachloride mixture. These observed values are higher than the calculated value, but it seems certain that the unit cell contains two formula units.

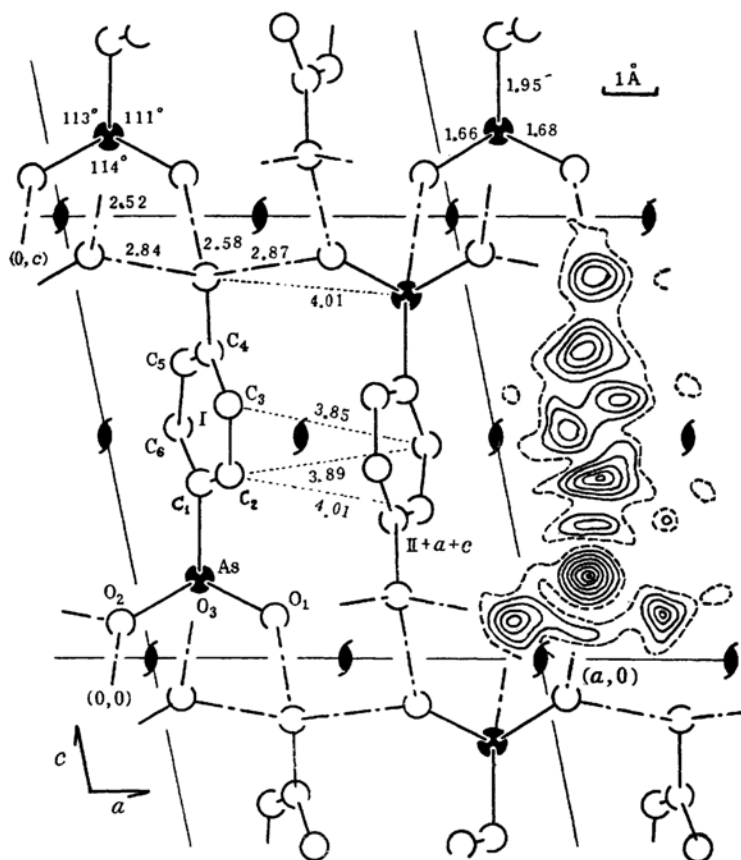


Fig. 2. The structure and the electron-density projection along the  $b$  axis, with bond angles, intra- and intermolecular distances (Å). Contours at intervals of  $2\text{e}\text{\AA}^{-2}$ , starting at  $2\text{e}\text{\AA}^{-2}$  (broken lines), except the arsenic atom, where contours are at intervals of  $10\text{e}\text{\AA}^{-2}$ . Dot-dash lines indicate hydrogen bonds.

no absorption corrections were applied. The corrections for polarization and Lorentz factors were made in the usual way.

### Structure Determination

The structure has been determined by making use of the heavy atom technique. The Patterson projection  $P(UW)$  onto the (010) plane was first synthesized, because the  $b$  axis is the shortest and the projection of the structure has a center of symmetry. This Patterson projection  $P(UW)$ , as shown in Fig. 1a, seemed to give some clues to the outline of molecules due to vectors from the heavy arsenic atom to the lighter atoms in addition to the location of the arsenic atom due to the large rotation peak near the origin. Consequently, we set up the minimum function  $M_2(XZ)$  based upon this rotation peak. At the same time, the electron-density projection  $\rho_1(XZ)$  was synthesized, the Fourier terms being the observed structure amplitudes whose

signs were determined only by the coordinates of an arsenic atom. It will be seen that there is a good correspondence between  $M_2(XZ)$  and  $\rho_1(XZ)$  as shown in Figs. 1b and 1c, and they are sufficient to give the approximate coordinates of lighter atoms. With these maps as a start, a sequence of electron-density projections were synthesized to make clear all of the atomic positions except hydrogen atoms.

Although the projection onto (100) plane has no center of symmetry, the electron-density projections were constructed by the successive refining, referring to the Patterson projection onto (100) plane and the refined electron-density projection onto (010) plane. The final electron-density projections are shown in Figs. 2 and 3, and the final coordinates are listed in Table I, being refined by the difference syntheses at later stages.

In the calculation of structure factors, McWeeny's scattering curves<sup>3)</sup> for nitrogen

3) R. McWeeny, *Acta Cryst.*, 4, 513 (1951).

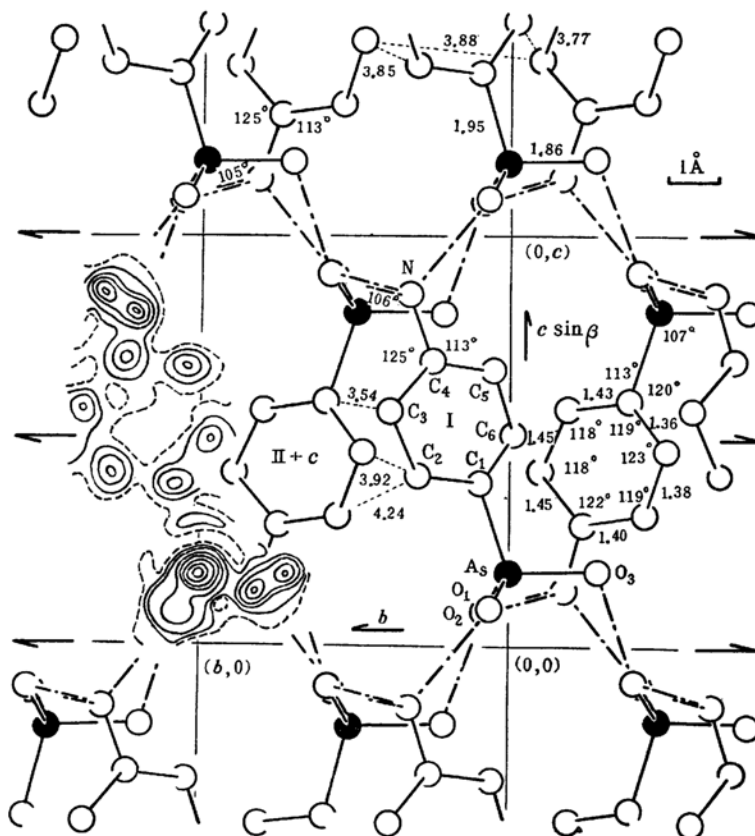


Fig. 3. The structure and the electron-density projection along the *a* axis, with bond angles, intra- and intermolecular distances (Å). Contours at intervals of  $2e\text{\AA}^{-2}$ , starting at  $2e\text{\AA}^{-2}$  (broken lines), except the vicinity of the arsenic atom, where contours above  $6e\text{\AA}^{-2}$  are at intervals of  $10e\text{\AA}^{-2}$ . Dot-dash lines indicate hydrogen bonds.

TABLE I. ATOMIC COORDINATES

| Atom           | <i>x/a</i>         | <i>y/b</i> | <i>z/c</i>         |
|----------------|--------------------|------------|--------------------|
| As             | 0.163 <sub>2</sub> | 0          | 0.183 <sub>1</sub> |
| O <sub>1</sub> | 0.338              | 0.063      | 0.093              |
| O <sub>2</sub> | -0.041             | 0.078      | 0.086              |
| O <sub>3</sub> | 0.156              | -0.293     | 0.185              |
| C <sub>1</sub> | 0.213              | 0.093      | 0.398              |
| C <sub>2</sub> | 0.299              | 0.295      | 0.418              |
| C <sub>3</sub> | 0.331              | 0.386      | 0.572              |
| C <sub>4</sub> | 0.298              | 0.254      | 0.698              |
| C <sub>5</sub> | 0.234              | 0.047      | 0.675              |
| C <sub>6</sub> | 0.184              | -0.028     | 0.523              |
| N              | 0.327              | 0.318      | 0.863              |

atom, of "valence states" for carbon atom and of  $1/3(f^{\parallel} + 2f^{\perp})$  for oxygen atom were used, while the scattering curve given by Berghuis et al.<sup>4)</sup> was used for arsenic atom. An isotropic temperature factor was estimated to be  $2.7\text{\AA}^2$  for all atoms. *R* indicates for the

final coordinates were 13.0 and 14.9% for (*h*0*l*) and (0*k**l*) respectively, excluding terms too weak to be observed. The comparison of observed structure factors with calculated ones is shown in Fig. 4.

### Description of the Structure

The general nature of the structure is shown in Figs. 2 and 3, which are *b* and *a* axis projections for this crystal. The arsenic atom is surrounded by a group consisting of three oxygen atoms, O<sub>1</sub>, O<sub>2</sub> and O<sub>3</sub> of the arsonic acid and one carbon atom C<sub>1</sub> of the benzene ring. The average As-O distance is 1.73 Å, and the As-C distance is 1.95 Å. The disposition of bonds from the arsenic atom appears to be nearly tetrahedral, the angles between the bonds being about 109°. The benzene ring is planar and the average distance between adjacent carbon atoms is 1.41 Å, individual values ranging from 1.36 to 1.45 Å. The N-C distance is 1.49 Å and the nitrogen atom is found to lie on the plane of a benzene ring

4) J. Berghuis, I. M. Haanappel, M. Poters, B. O. Loopstra, C. H. MacGillavry and A. L. Veenendaal, *ibid.*, 8, 478 (1955).

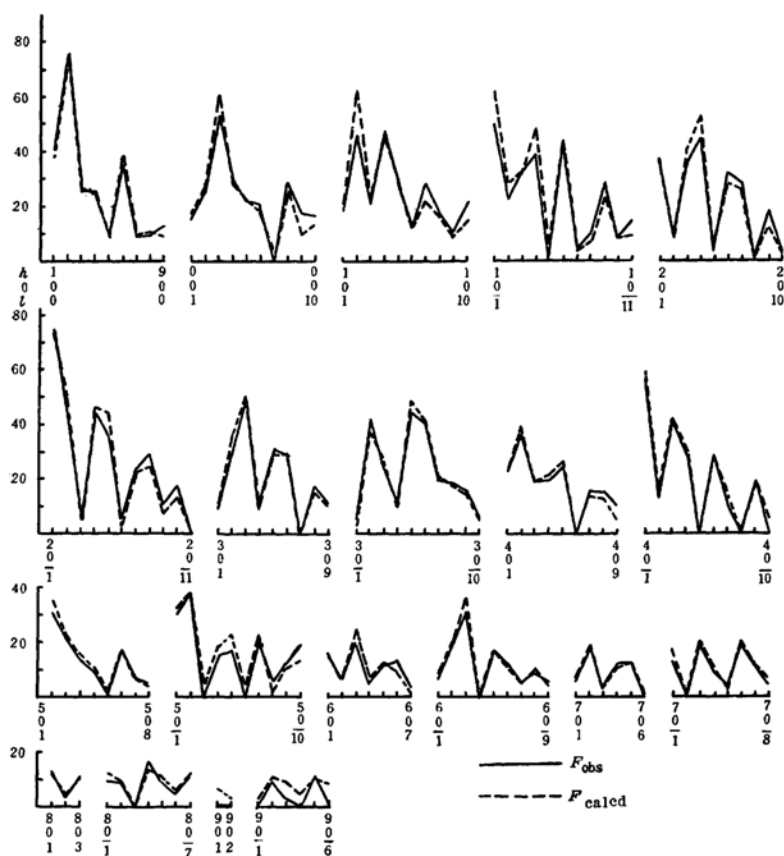


Fig. 4. (a) Comparison of observed and calculated structure factors,  $F(h0l)$ .

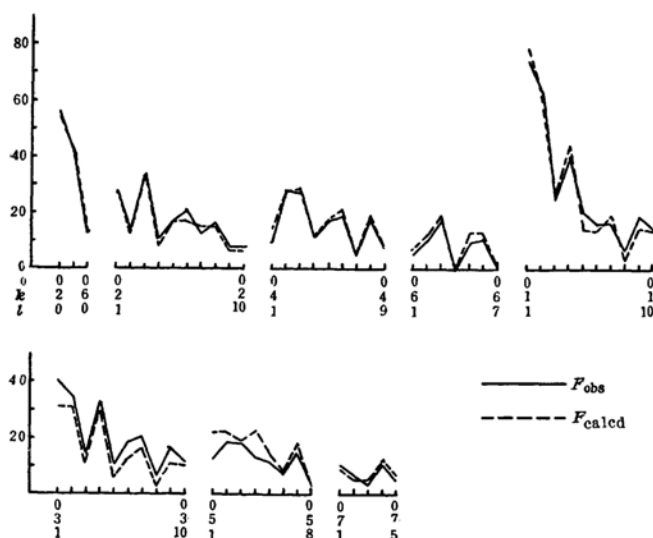


Fig. 4. (b) Comparison of observed and calculated structure factors,  $F(0kl)$ .

within the limit of experimental error.

The molecules are held together by a beautiful network of hydrogen bonds. These are four hydrogen atoms available for hydrogen bonding in an asymmetric unit. Two of them come from the *p*-amino group, two come from the arsonic group. There is one hydrogen bond between oxygen atoms and there are three hydrogen bonds between oxygen and nitrogen atoms. The hydrogen bond, with a length 2.52 Å from the atom O<sub>2</sub> of molecule I to the atom O<sub>3</sub> of molecule II, links molecules with each other to form endless chains along the screw axis perpendicular to the (010) plane. The nitrogen atom in the *p*-amino group of the molecule I forms three hydrogen bonds, the first with a length 2.84 Å to the atom O<sub>2</sub> of the molecule II + *c* (molecule displaced by the unit vector *c*), the second with a length 2.58 Å to the atom O<sub>1</sub> of the molecule I + *c*, and the third with a length 2.87 Å to the atom O<sub>1</sub> of the molecule II + *a* + *c*. These three hydrogen bonds connect the endless chains through benzene rings to form a three dimensional net work. This triple hydrogen-bond formation of a nitrogen atom will suggest that one of hydrogen atoms is transferred from an arsonic acid group to the *p*-amino group. On this basis, the formula of the molecule should be written as NH<sub>3</sub><sup>+</sup>·C<sub>6</sub>H<sub>4</sub>·AsO<sub>2</sub>(OH)<sup>-</sup>, which indicates that the molecule is in the zwitterion form in the crystal. This conclusion will be supported by the fact that this acid is strictly monobasic<sup>5)</sup>.

There is no seriously short van der Waals contact in this structure. The shortest distance

between neighboring molecules, 3.51 Å, is found between the atom O<sub>2</sub> of the molecule I and the arsenic atom of the molecule II. There is also a contact at 3.54 Å between the atom O<sub>1</sub> of the molecule I and the atom C<sub>4</sub> of the molecule II + *a* + *c* - *b*. The shortest contact between adjacent benzene rings occurs at 3.54 Å between the atom C<sub>1</sub> of the molecule I and the atom C<sub>3</sub> of the molecule II + *a* + *c* - *b*. Other intermolecular distances exceed 3.55 Å. A comparison of this structure with that of the benzenearsonic acid is interesting. They are closely similar in having endless chains formed by the hydrogen bonds between arsonic acid groups, while in *p*-aminobenzenearsonic acid there are additional hydrogen bonds to connect these chains. This difference in mode of packing will explain why the crystal of *p*-aminobenzenearsonic acid has no cleavage, in contrast to that of benzenearsonic acid which shows cleavages along endless chains.

The author wishes to express his sincere thanks to Professor I. Nitta and Professor T. Watanabé of Osaka University for their helpful advice, and to Professor H. Nakata of Konan University for supplying the specimens.

*Department of Chemistry  
Faculty of Science  
Osaka City University  
Kita-ku, Osaka*

---

5) A. E. Goddard, "A Text-book of Inorganic Chemistry", Vol. XI., Part II, Charles Griffin and Co., London (1930), p. 179.