The Crystal Structure of m-Aminobenzenearsonic Acid[*]

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The crystal and molecular structure of benzenearsonic acid and its *p*-amino derivative have been recently investigated by the present author[1,2]. These two structures are closely related in both having endless chains formed by the hydrogen bonds between arsonic acid groups, although the molecule in the latter is to be regarded as a zwitterion and although the $-NH_3^+$ group in this ion forms additional hydrogen bonds to link the chains. In connection with the above work, the crystal structure of *m*-aminobenzenearsonic acid, $H_2N\cdot C_6H_4AsO(OH)_2$, was examined as part of a program to contribute to the structural chemistry of organoarsenic compounds.

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[*] The major part of this papar was read at the 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961.

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

[2] A. Shimada, ibid., 34, 639 (1961).

Experimental

Crystals suitable for X-ray work were selected from specimens kindly prepared and supplied by Prof. H. Nakata of Konan University. They were colorless, transparent, and lath-like needles with a long dimension in the c direction. The crystals used in this experiment had square cross sections 0.16×0.15 mm. for $(h\,k\,0)$, 0.22×0.24 mm. for $(0\,k\,l)$, and 0.26×0.29 mm. for $(h\,0\,l)$. Oscillation and Weissenberg photographs around three principal axes were taken with CuK_α radiation; it was found from an examination of them that the unit cell is monoclinic with the following dimensions:

$a=13.35$, $b=15.60$, $c=7.46$ Å and $\beta=92.7°$

This choice of axes, which makes the unit cell base-centered, is unconventional in the case of the monoclinic system, but the crystal was referred to these axes for the sake of experimental convenience, since the c axis lies along a needle direction and since the a axis is almost perpendicular to the needle direction by this choice of axes. The cell size of this crystal gave a calculated density of 1.857 g. cm^{-3} on the assumption that there are eight formula units in a unit cell. This calculated density is close to the value found for the *p*-amino derivative.

The extinctions observed, $h\,k\,l$ when $h+l$ is odd, $h\,0\,l$ when h and l is odd, and $0\,k\,0$ when k is odd, indicate that the space group is $C_{2h}^5-B2_1/a$. By comparing these results with a calibrated scale, visual intensity measurements were made with the aid of both multiple exposure and multiple-film techniques. They were corrected for the appropriate Lorentz and polarization factors, and the correction for absorption ($\mu=58.6$ cm^{-1}) was evaluated on the assumption that the specimens were cylindrical rods.

Structure Determination

The structure was determined by making use of the heavy atom technique. Thus, the Patterson projection $P(UV)$ along the c axis was first synthesized because of the short c axis. In this projection were found trains of peaks along the b axis at approximately $U=0$ and $U=a/4$ due to vectors from the heavy arsenic atom to the lighter atoms; peaks due to vectors between arsenic atoms were also found. This striking appearance suggests that the planes of benzene rings are perhaps almost parallel to the (100) plane and pack one above the other, with a separation of one quarter of a period along the a axis. This fact was confirmed by the minimum function based on the rotation peak between arsenic atoms and also by the preliminary electron-density map, the Fourier terms of which were observed structure amplitudes with signs determined only by the approximate coordinates of arsenic atoms derivable from the Patterson function. Hence, it was not so difficult to locate plausible positions of the lighter atoms in this projection with this feature of the packing mode of benzene rings, although there was a heavy overlapping of the carbon atoms of benzene rings.

Referring to this feature of the structure, the Patterson and electron-density maps along the a axis were synthesized by the same procedure. These two maps along the a axis, together with the aid of the projection along the c axis, were sufficient to give all of the atomic positions except those of the hydrogen atoms; the projection along the b axis was also tried in order to confirm the atomic positions derived by the other projections.

Refinement of the coordinates of atoms was carried out by successive Fourier syntheses and also by difference syntheses at later stages. In the calculation of the structure factors, McWeeny's scattering curves[3] for the nitrogen atom, of " valence states " for carbon and of $1/3(f^{\parallel}+2f^{\perp})$ for the oxygen atom, were used,

TABLE I. ATOMIC COORDINATES

Atom	x/a	y/b	z/c
As	0.087_4	0.162_5	0.135_1
O_1	0.172	0.238	0.215
O_2	−0.040	0.196	0.136
O_3	0.112	0.138	−0.092
C_1	0.111	0.059	0.268
C_2	0.109	−0.022	0.184
C_3	0.130	−0.092	0.300
C_4	0.137	−0.089	0.488
C_5	0.141	−0.008	0.563
C_6	0.124	0.061	0.457
N	0.143	−0.179	0.221

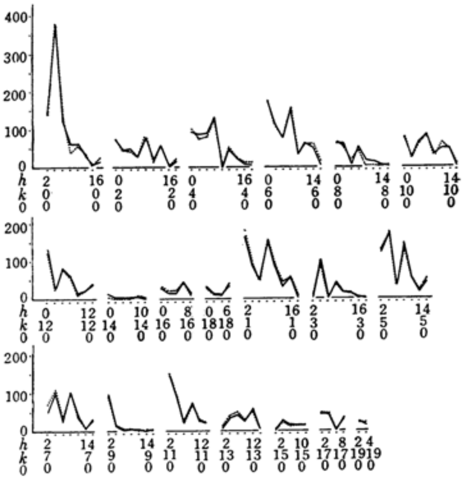

Fig. 1a. Comparison of observed and calculated structure factors, $F(h\,k\,0)$.
—— F_{obs} …… F_{calcd}

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

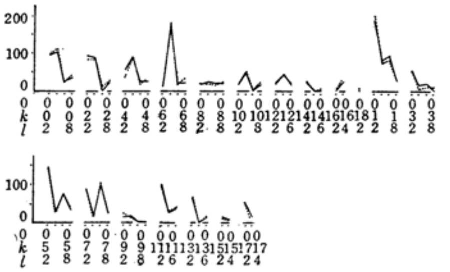

Fig. 1b. Comparison of observed and calculated structure factors, $F(0kl)$.
—— F_{obs} …… F_{calcd}

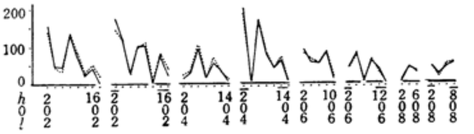

Fig. 1c. Comparison of observed and calculated structure factors, $F(h0l)$.
—— F_{obs} …… F_{calcd}

while that given by Berghuis et al.[4] was used for the arsenic atom. The isotropic temperature factors were estimated to be 2.7Å^2 for all atoms. The R indices for the final coordinates listed in Table I were 10.0, 11.8 and 11.6% for $(hk0)$, $(0kl)$ and $(h0l)$ respectively, excluding terms too weak to be observed. The observed structure factors are compared with those calculated in Fig. 1.

Description of the Structure

The configuration of a molecule and the molecular arrangement in the crystal may be seen in Figs. 2a, 2b and 2c, which represent the c, a and b axes projections for this crystal. The arsenic atom is surrounded by a group of three oxygen atoms, O_1, O_2 and O_3 of the arsonic acid, and one carbon atom C_1 of the benzene ring. The average As–O distance is 1.76 Å, and the As–C distance is 1.91 Å. The disposition of bonds from the arsenic atom appears to be nearly tetrahedral, the angles between the bonds being about 110°. The benzene ring is planar, and the average distance between adjacent carbon atoms is 1.39 Å, individual values ranging from 1.35 Å to 1.41 Å. The N–C distance is 1.49 Å, and the nitrogen atom is found to lie on the plane of a benzene ring within the limit of experimental error. This molecular configuration is considered to be in accordance with those of benzenearsonic acid and its p-amino derivative.

The molecules are held together by a beautiful network of hydrogen bonds. There are four hydrogen atoms available for hydrogen bonding in an asymmetric unit. Two of them come from the m-amino group, and two come from the arsonic acid group. There is one hydrogen bond between oxygen atoms, and there are three hydrogen bonds between oxygen and nitrogen atoms in the crystal. The hydrogen bond, with a length of 2.56 Å from the O_3

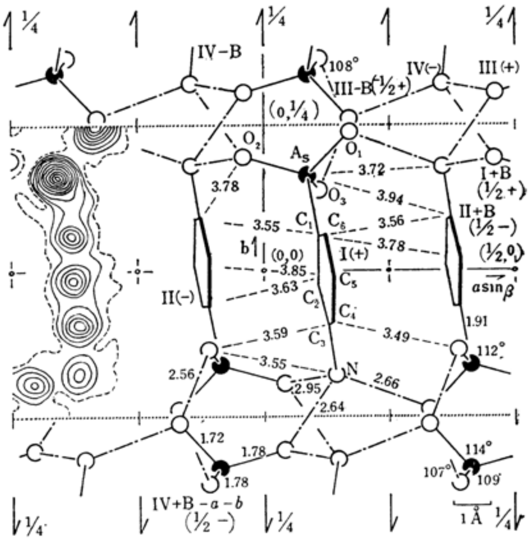

Fig. 2a. The structure and the electron-density projection along the c axis, with bond angles, intra- and intermolecular distances (Å). Contours at arbitrary scale. Dot-dash lines indicate hydrogen bonds.

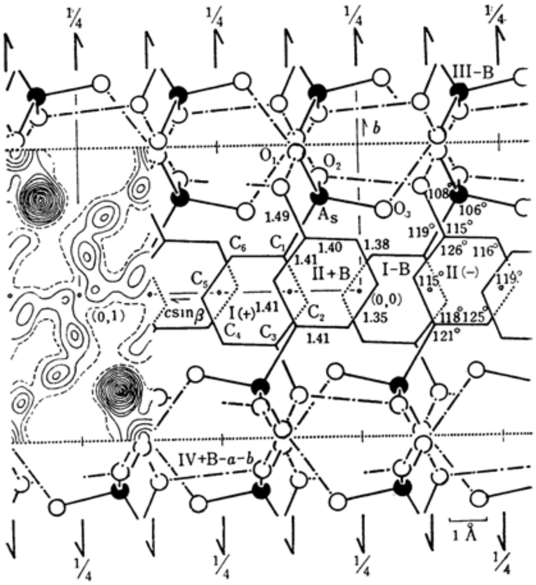

Fig. 2b. The structure and the electron-density projection along the a axis, with bond angles and intramolecular distances (Å). Contours at arbitrary scale. Dot-dash lines indicate hydrogen bonds.

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[4] J. Berghuis, I. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry and A. L. Veenedaal, ibid., 8, 478 (1955).

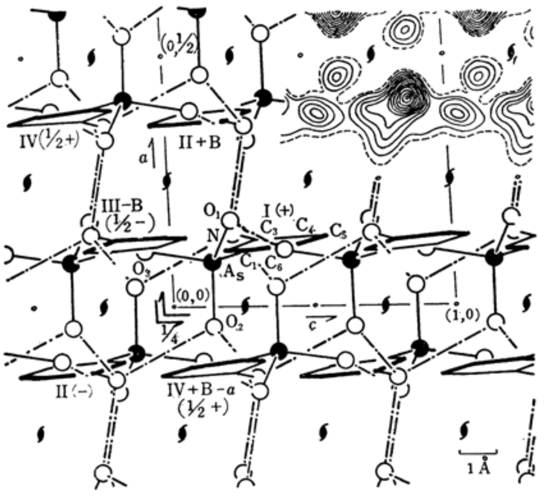

Fig. 2c. The structure and the electron-density projection along the b axis. Contours at arbitrary scale. Dot-dash lines indicate hydrogen bonds.

atom of I molecule to the O_1 atom of the III−B molecule, links the molecules with each other to form endless chains along the c axis. The nitrogen atom in the *m*-amino group of molecule I forms three hydrogen bonds, the first with a length of 2.95 Å to the O_2 atom of II molecule, the second with a length of 2.64 Å to the O_2 atom of IV+B−a−b molecule, and the third with a length of 2.66 Å to the O_1 atom of the II+B molecule. This triple hydrogen-bond formation of a nitrogen atom suggests that one of the hydrogen atoms is transferred from an arsonic acid group to the *m*-amino group. On this basis, the formula of the molecule should be written as $NH_3^+ \cdot C_6H_4 \cdot AsO_2(OH)^-$, which indicates that the molecule is in the zwitterion form in the crystal.

Three hydrogen bonds around a nitrogen atom connect the chains mentioned above to form a sheet which is perpendicular to the b axis and is located around a glide plane. These sheets of hydrogen bonds are interlocked through the benzene rings, which are found to stack with each other along the a axis. This mode of packing of the molecule is similar to that of *p*-aminobenzenearsonic acid, while only hydrogen-bonded chains are packed together by van der Waals forces in benzenearsonic acid. All the intermloecular distances correspond to normal van der Waals interactions; the shorter contacts are illustrated in Fig. 2.

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