The Crystal Structure of Phenylarsonic Acid[1]

By Akira SHIMADA

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The chemistry of organoarsenic compounds has an earlier growth than that of others among those of organometallic compounds, and this fact has again attracted much attention of chemists in recent days[2]. However, there are only a few structural studies of the organoarsenic compounds[3-10], and, hence, it may be of interest and importance in this field of chemistry to reveal the spatial configuration and orientation of the molecules in the crystal of phenylarsonic acid, $C_6H_5AsO(OH)_2$, which is one of the fundamental compounds in the organoarsenic compounds. The present work, which provides the first determination of the packing mode of organoarsonic acid, seems of interest also from the standpoint of the hydrogen-bond formation, in comparison with other organic acids.

Experimental

In a preliminary note, the crystallographic constants were already reported[1]; the crystal of this compound belongs to the orthorhombic system and the space group $D_2^4-P2_12_12_1$ with four chemical units in a unit cell, which has the following dimensions;

$a=10.42\pm0.02$, $b=14.92\pm0.02$, $c=4.70\pm0.02$ Å

The data mentioned above are in fairly good agreement with those recently reported by Bryden[11]. Oscillation and Weissenberg photographs were taken around the principal axes with Cu $K\alpha$ radiation. Intensities were obtained by the multiple-film technique in Weissenberg photographs and were estimated by visual comparison with a calibrated scale. They were corrected by means of the usual Lorentz and polarization factors, while the correction for absorption was evaluated under the assumption that the specimens were cylindrical rods. The absorption effect could not be neglected, especially for $(0\,k\,l)$ and $(h\,0\,l)$ spectra because of the rather high absorption coefficient ($\mu=60.3\ \text{cm}^{-1}$) of the crystals and because of their dimensions [cross section with rectangular dimensions: 0.20×0.25 mm. for $(h\,k\,0)$, 0.65×0.40 mm. for $(0\,k\,l)$, and 0.70×0.65 mm. for $(h\,0\,l)$].

Structure Determination

The structure has been determined by making use of the heavy-atom technique. Thus, the electron density projection $\rho(xy)$, favorable because of the short c axis, were fairly well resolved to reveal the configuration of the molecules, as described in the preliminary note[1]. The electron density projections $\rho(yz)$ and $\rho(xz)$ were easily constructed by the same method, referring to the refined electron density projection $\rho(xy)$. These projections were shown in Figs. 1—3, and the final coordinates are listed in Table I, their refinement being made by the difference syntheses at later stages. In the calculation of structure factors, McWeeny's scattering curves[12] 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.[13] was used for arsenic atom. Isotropic temperature factors were estimated to be 3.3 Å^2

TABLE I. ATOMIC COORDINATES

Atom	x/a	y/b	z/c
As	0.334_4	0.126_5	0.211_2
O_1	0.457	0.111	−0.032
O_2	0.192	0.109	0.079
O_3	0.372	0.060	0.499
C_1	0.338	0.249	0.320
C_2	0.429	0.313	0.218
C_3	0.424	0.400	0.332
C_4	0.336	0.423	0.531
C_5	0.249	0.360	0.633
C_6	0.242	0.271	0.520

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[1] A preliminary account has already appeared in This Bulletin, **32**, 309 (1959).

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[11] J. H. Bryden, ibid., **12**, 558 (1959).

[12] R. McWeeny, ibid., **4**, 513 (1951).

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

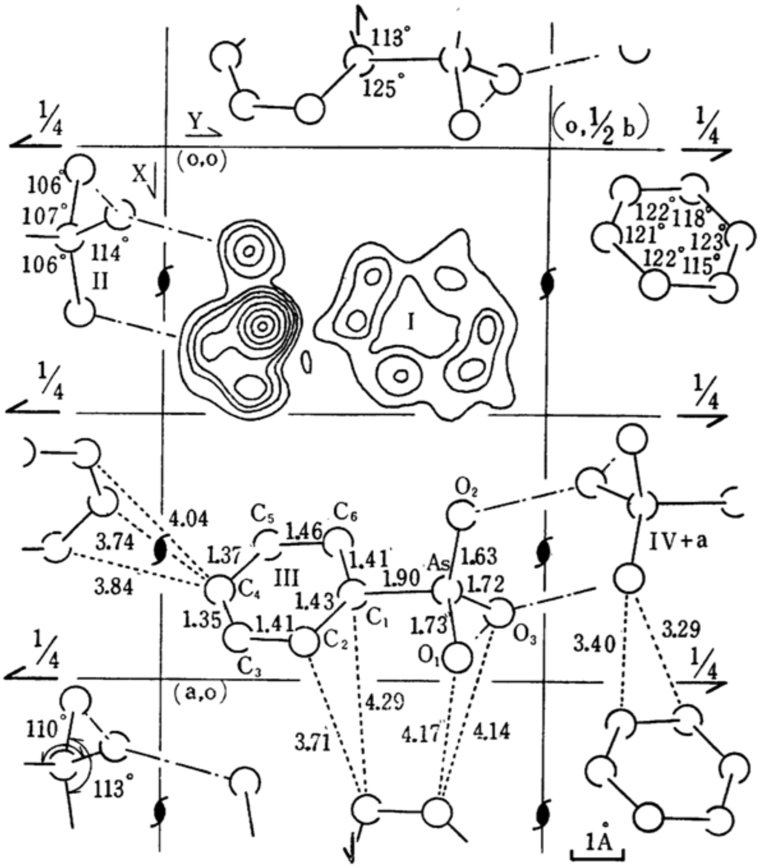

Fig. 1. The structure and the electron-density projection along the c axis, with bond angles, intra- and intermolecular distances (Å). Contours at intervals of 2 eÅ^{-2}, starting at 2 eÅ^{-2}, except at the arsenic atom, where contours above 8 eÅ^{-2} are at intervals of 10 eÅ^{-2}. Dot-dash lines indicate hydrogen bonds.

for all atoms in the case of ($h\,k\,0$) and ($0\,k\,l$), and 4.2 Å^2 in the case of ($h\,0\,l$). R indices for the final coordinates were 18.0, 14.0 and 15.6%, for ($h\,k\,0$), ($0\,k\,l$) and ($h\,0\,l$), respectively, excluding terms too weak to be observed.

Description of the Structure

The general nature of the structure is shown in Figs. 1—3, which are c, a and b axis projections for this compound. The aresenic atom is surrounded by a group consisting 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 1.69 Å, and the As-C distance is 1.90 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 planer and the averge distance between adjacent carbon atoms is 1.41 Å, individual values ranging from 1.35 to 1.46 Å.

Phenylarsonic acid, which has two active hydrogen atoms, forms two hydrogen bonds, one with a length 2.64 Å from the atom O_3 of molecule I to the atom O_2 of molecule II, the other with a length 2.49 Å from the atom O_3 of molecule I to the atom O_1 of molecule I+c (molecule displaced by the unit vector c). This arrangement of these two types of hydrogen bonds links molecules with each other to form endless chains along the twofold axis perpendicular to the (001) plane. The benzene rings are connected through the arsenic atom to these chains which are held together by the van der Waals force only. The shorter distances between neighboring molecules occur between O_2 of one molecule and C_2, O_3 and C_3 of adjacent molecules; these distances are 3.29, 3.39 and 3.40 Å, respectively. Other intermolecular distances exceed 3.71 Å.

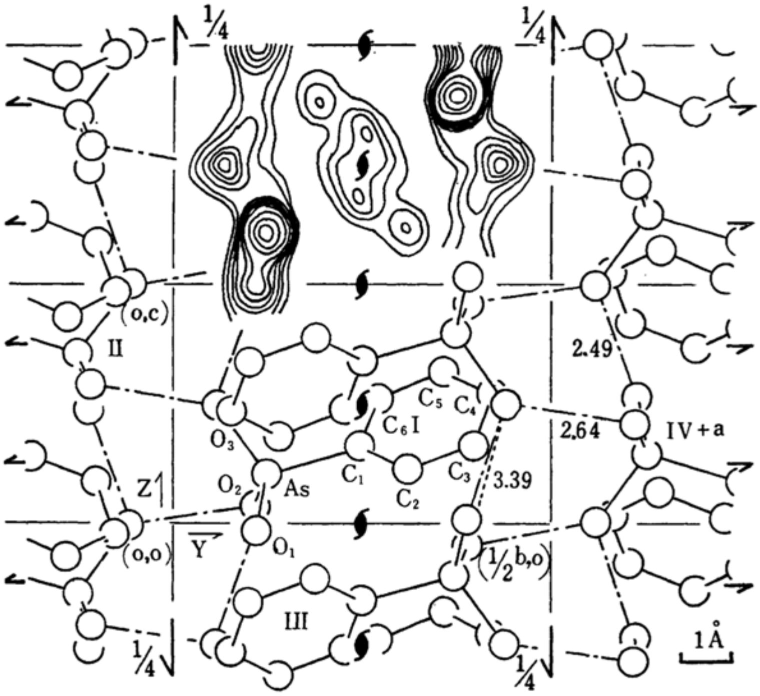

Fig. 2. The structure and the electron-density projection along the *a* axis, with intermolecular distances (Å). Contours at intervals of 2 $eÅ^{-2}$, starting at 4 $eÅ^{-2}$, except at the arsenic atoms, where contours above 16 $eÅ^{-2}$ are at intervals of 10 $eÅ^{-2}$. Dot-dash lines indicate hydrogen bonds.

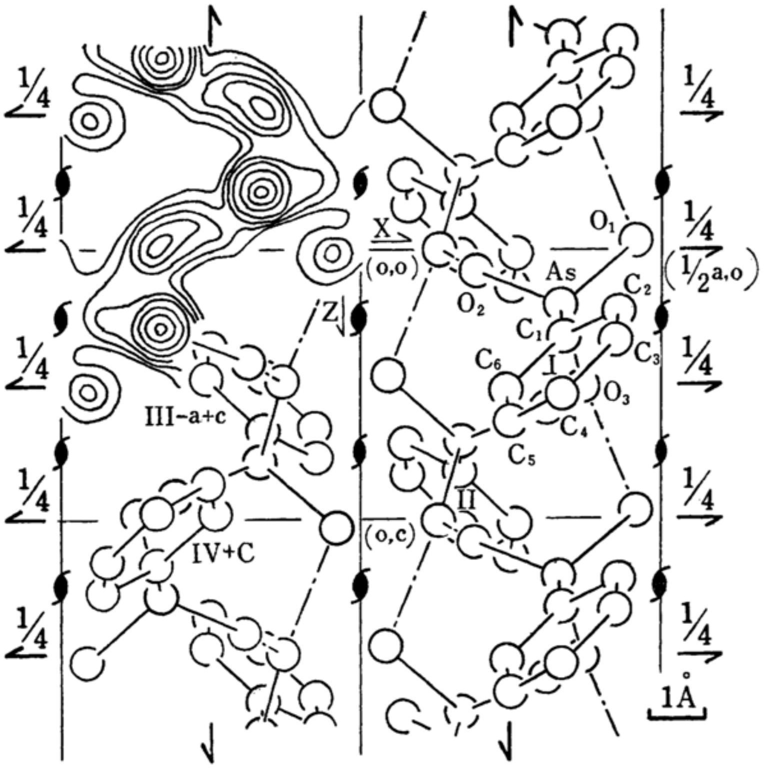

Fig. 3. The structure and the electron-density projection along the *b* axis. Contours at intervals of 3 $eÅ^{-2}$, starting at 5 $eÅ^{-2}$, except at the arsenic atoms, where contours above 11 $eÅ^{-2}$ are at intervals 10 $eÅ^{-2}$. Dot-dash lines indicate hydrogen bonds.

This mode of packing the molecules would explain the cleavages along the planes parallel to the (110) and (100) planes.

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Department of Chemistry
Faculty of Science
Konan University
Higashinada, Kobe