*The Crystal Structure of Phenylarsonic Acid**

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(Received December 28, 1958)

In the attempt to determine the molecular configuration of an organoarsenic compound and at the same time to compare the structure of this acid with that of other organic acids, this study was undertaken. Small needle crystals of phenylarsonic acid, $C_6H_5AsO(OH)_2$, were easily obtained by the slow evaporation of a water-ethanol solution. Oscillation and Weissenberg photographs prepared with Cu K_α radiation gave the following unit-cell dimensions:

$$a=10.42, \quad b=14.92, \quad c=4.70\ \text{Å}$$

Schröder et al.[1] already showed that this crystal was orthorhombic with the axial ratios 0.7048 : 1 : 0.203, and also that perfect cleavages were found along the (110) plane, and imperfect ones along the (100) plane. The axial ratios given by these authors can be compared with the values derived by the X-ray measurement, 0.698 : 1 : 0.315 = 0.698 : 1 : 0.210×3/2. With assumption of four chemical units in the unit cell with the dimension given above, one can calculate the density to be 1.84 g./cc., which agrees satisfactorily with the observed value, 1.804 g./cc., reported by Schröder[2]. The systematic absence of (h00) reflections for h=odd, (0k0) ones for k=odd, (00l) ones for l=odd, and nothing else lead to the space group D^4_{42}–$P2_12_12_1$. Intensities were estimated visually with a calibrated scale, by making use of the multiple-film technique. The corrections for polarization and Lorentz factors were made in the usual way and that for absorption was neglected.

Since the c axis is shorter and each projection has the center of symmetry with plane group P_{gg}, the Patterson projection onto the (001) plane was first synthesized, which revealed clearly interatomic vectors between arsenic atoms owing to their greater scattering powers. The first electron-density projection was then synthesized, the Fourier coefficients being the observed structure amplitudes $|F_{hk0}|$'s with the signs determined by the arsenic atoms alone, and the successive refinement of the electron-density projection made clearer all of the atomic positions except hydrogen atoms. The electro-density projection is shown in Fig. 1. The reliability index for (hk0) spectra is, at the present stage of refinement, 20% with a temperature factor $B=4.2\ \text{Å}^{-2}$ for all. Preliminary studies of electron-density projections along other axes with the same method of analyses were sufficient to give an approximate z coordinate of each atom, from which the outline of the molecular configuration as well as their orientation were derived.

Although the result given above is preliminary and not very accurate, some interesting features of crystal structure were revealed. The interatomic distances within a molecule as well as between nearest molecules were found to be plausible. Three As–O bonds, with a mean length of 1.6_9 Å, and an As–C_1 bond, with a length of 1.9_1 Å, are arranged in a distorted tetrahedron. Long chains are formed along the two-fold screw axis perpendicular to the (001) plane by two sets of non-equivalent hydrogen bonds $-OH_1\cdots O_3\cdots HO_2-$. One set of hydrogen bonds with

* The major part of this paper was read at the Autumnal Joint Meeting of Chemical Societies of Japan, Tokyo, 1958.

1) P. Groth, "Chemische Krystallographie", Bd. IV, 354, Engelmann Leipzig, (1917).

2) Schröder, *Ber.*, **12**, 562 (1879).

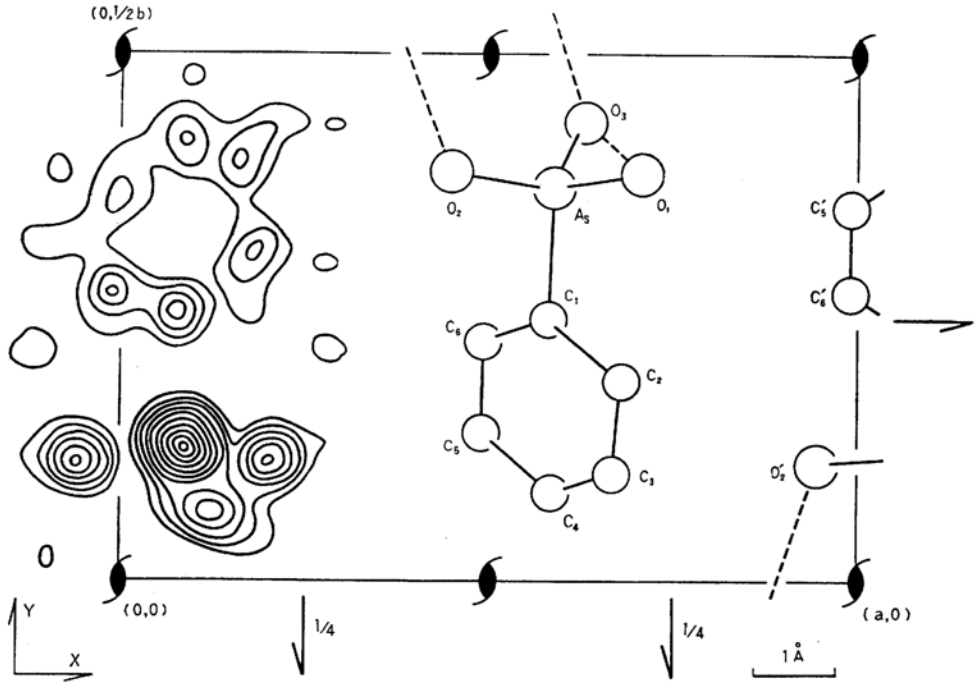

Fig. 1. Projection of the structure on (001). Contours are drawn at arbitrary intervals. Dashed line indicates the hydrogen bond between the molecules.

a distance 2.7_3 Å unites the oxygens, O_2 and O_3, of adjacent molecules around the screw axis, while the other set with a distance 2.5_6 Å unites the oxygens, O_3 and O_1, of adjacent molecules both along the *c* axis. The benzene rings are connected through the arsenic atoms to these chains and, hence, there might be no intermolecular forces other than those of the van der Waals type between these chains. This mode of packing of the molecules would explain the cleavages along the planes parallel to the (110) and (100) planes. Further refinement of the structure is now in progress.

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

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