CRYSTAL AND MOLECULAR STRUCTURE OF PHENYLARSONIC ACID

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Deciphering of the structure. The crystals of phenylarsonic acid \( \text{C}_6\text{H}_4\text{AsO(OH)}_2 \) used by us for an x-ray study of the structure, represent very fine yellow needles with a length up to 5 mm and a cross section of \( \sim 0.1 \cdot 0.1 \) mm. The needles are bounded by the four faces of a rhombic prism \( \{201\} \) (\( b \) is the axis of the needles); the faces of the heads are not expressed. The parameters of the unit cell were determined by the oscillation method and the density was determined by hydrostatic weighing.

\[
\begin{align*}
\text{a} &= 14.74 \pm 0.05 \text{ Å} \\
\text{b} &= 4.65 \pm 0.01 \text{ Å} \\
\text{c} &= 10.38 \pm 0.02 \text{ Å} \\
\text{V} &= 711 \pm 3 \text{ Å}^3
\end{align*}
\]

\[M = 202.03\]

\[d_{\text{meas}} = 1.86 \text{ g/cm}^3\]

\[d_{\text{x-ray}} = 1.90 \text{ g/cm}^3\]

\[n = 3.92(4) \text{ C}_6\text{H}_4\text{AsO(OH)}_2\]

Systematic extinctions of the reflections of type \( h00 \) at \( h \neq 0k0 \), \( 0k0 \) at \( k \neq 2n \) and \( 00l \) at \( l \neq 2n \), and the presence of piezoelectric properties, clearly define the space group \( \text{P}2_12_12_1 \).

To determine the coordinates of the atoms, the \( h0l \) and \( hkl \) scans, respectively, containing 125 and 51 reflections of the measured intensity, were obtained when the reciprocal lattice was photographed (unfiltered Mo-radiation). The photographing was done using a backing of three films; in computing the intensities of the structure factors the Lorentz and polarization factors were taken into account, while the correction for absorption was neglected. The coordinates of the As atom were found from the \( ac \) and \( ab \) projections of the interatomic function. They were used to determine the first series of signs of the structure amplitudes. The subsequently computed projections of the electron density on the same faces of the cell disclosed all of the atoms of the molecule except hydrogen. The second series of signs was now found, taking into consideration all of the atoms, in which connection for C and O we used the atomic curves of Viervoll and Ogrim, and for As the curve from the "International Tables". These signs were used to compute the second approximation of the projections of the electron density. The coordinates from the second approximation led to the same signs, so that this approximation proves to be final. The structure amplitudes calculated from these coordinates were used to calculate the theoretical projections of the electron density, serving for introduction of the correction for Buse break in the coordinates of the second approximation; the final values of the coordinates, given in Table 1, were obtained in the same manner. In all cases the coordinates of the maxima were determined by exponential interpolation.

**TABLE 1. Relative Coordinates of Atoms**

<table>
<thead>
<tr>
<th>Atom</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>Atom</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{As} )</td>
<td>0.1262</td>
<td>0.4449</td>
<td>0.0848</td>
<td>( \text{C}_6 )</td>
<td>0.307</td>
<td>0.370</td>
<td>0.474</td>
</tr>
<tr>
<td>( \text{O}_1 )</td>
<td>0.109</td>
<td>-0.032</td>
<td>-0.063</td>
<td>( \text{C}_4 )</td>
<td>0.311</td>
<td>0.243</td>
<td>0.175</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>0.057</td>
<td>0.400</td>
<td>0.121</td>
<td>( \text{H}_2 )</td>
<td>0.220</td>
<td>0.591</td>
<td>-0.079</td>
</tr>
<tr>
<td>( \text{O}_3 )</td>
<td>0.111</td>
<td>-0.120</td>
<td>0.203</td>
<td>( \text{H}_3 )</td>
<td>0.372</td>
<td>0.815</td>
<td>-0.081</td>
</tr>
<tr>
<td>( \text{C}_3 )</td>
<td>0.247</td>
<td>0.323</td>
<td>0.084</td>
<td>( \text{H}_4 )</td>
<td>0.486</td>
<td>0.673</td>
<td>0.081</td>
</tr>
<tr>
<td>( \text{C}_4 )</td>
<td>0.269</td>
<td>0.529</td>
<td>-0.009</td>
<td>( \text{H}_5 )</td>
<td>0.446</td>
<td>0.308</td>
<td>0.245</td>
</tr>
<tr>
<td>( \text{C}_5 )</td>
<td>0.355</td>
<td>0.656</td>
<td>-0.019</td>
<td>( \text{H}_6 )</td>
<td>0.294</td>
<td>0.084</td>
<td>0.247</td>
</tr>
<tr>
<td>( \text{C}_6 )</td>
<td>0.419</td>
<td>0.576</td>
<td>0.082</td>
<td>( \text{H}_7 )</td>
<td>0.306</td>
<td>0.084</td>
<td>0.247</td>
</tr>
</tbody>
</table>

*The coordinates of the hydrogen atoms were calculated using the conventional assumptions: C-H = 1.08 Å; C-C-H = 120°.*
A comparison of $F_{\text{meas.}}$ and $F_{\text{calcd.}}$, leads to the following authenticity factors and temperature corrections: projection ac-$R = 9.6\%$, $B = 3.47$ Å$^2$; projection ab-$R = 13.6\%$, $B = 3.65$ Å$^2$. Assuming that $R = b$ is the error of measuring the structure amplitudes, we find from the Weinstein equation the accuracy of determining the positions of the atoms: $\Delta s = 0.002$ Å, $\Delta s = 0.012$ Å, and $C = 0.017$ Å. This leads to the following errors in the bond lengths: $\Delta s = 0.012$ Å, $\Delta s = 0.017$ Å, and $C = 0.024$ Å. The valence angles are found with an accuracy of $\pm 2^\circ$.

The chemical identity of the investigated compound, originally erroneously assumed to be arsenobenzene ($C_6H_5As$), was established in the present study. A deciphering of the structure was begun assuming that the crystals are arsenobenzene, but the projections of the electron density each disclosed three "superfluous" maxima in the vicinity of the As atom. These same maxima also appeared persistently in the different projections (with the exception of the As atom), so that it was impossible to doubt their reality. For this reason it became obvious that the starting arsenobenzene had undergone important chemical changes during the process of purification and recrystallization, and, specifically, had oxidized to phenylarsonic acid. The further deciphering of the structure was continued and was successfully consummated by considering the "superfluous" maxima to be O atoms. Thus, if they are not taken into consideration, then the authenticity factors increase sharply: $R_{	ext{sh}}$ from 9.6 to 24.7\%, and $R_{\text{sh}}$ from 13.6 to 24.9\%. In addition, the large difference in the calculated and measured densities becomes admissible, while the distance $\Delta s = \Delta s = 5.0$ Å does not correspond to a chemical bond.

The second approximation of the projections of the electron density on face ac is shown in Fig.1, where the maxima, corresponding to all the atoms of the phenylarsonic acid molecule, are seen distinctly.

*Fig.1. Second approximation of the ac projections of the electron density (relative units; the contour tour lines of the As atom are drawn half as often as in the other places).*

*Fig.2. Phenylarsonic acid molecule.*

The second approximation of the projections of the electron density in the phenylarsonic acid molecule, computed using the coordinates in Table 1, are shown in Fig. 2. The benzene ring is a flat rectilinear hexagon with sides equal to 1.40 Å. The valence angles $\angle_1 = 120^\circ$; the bond length $\Delta s = \Delta s = 1.97$ Å. In the literature [1] there are only two reliable measurements of the bond length $\Delta s = \Delta s = 1.30\pm 0.05$ Å in $C_6H_5As$ and $C_6H_5As$, which is in good agreement with our result, representing the first determination of the bond length between As and aromatic hydrocarbon. The lengths of the As=O bonds differ: $\Delta s = \Delta s = 1.75$ Å $\Delta s = \Delta s = 1.65$ Å. For this reason it is possible to assume that atoms $O_1$ and $O_2$ are found as hydroxyl groups, while atom $O_3$ forms a double bond with As. This assumption is also supported by the distribution of the hydrogen bonds in the structure (see below). According to the literature data [2], the length of the As=O bond varies from 1.75 to 1.80 Å, in which connection in most of the investigated objects this bond has an intermediate character (single-double), but hydrogen bonds are absent in the structures. The values of the atomic radii taken from Pauling lead to the following lengths of the single and double bonds: $\Delta s = \Delta s = 1.87$ Å, and $\Delta s = \Delta s = 1.65$ Å As a result, the length of the double bond $\Delta s = \Delta s = 0$ does not change when oxygen atoms take part in hydrogen bonds, while the single bond is shortened by 0.12 Å. An analogous effect was observed earlier in the structures of carboxylic acids having hydrogen bonds. Thus, for example, in the crystals of oxalic acid [3] and its dihydrate [4], C=O=1.29 Å instead of the sum of the radii 1.43 Å, while C=O=1.19 Å, with the sum of the radii equal to 1.25 Å.

The valence configuration of arsenic is approximately tetrahedral, with substantial deviations of the angles C–As–O and O–As–O from 109.5°:

- $C_1–As–O_1=109.0^\circ$, $O_1–As–O_2=117.0$ Å
- $C_2–As–O_3=101.0^\circ$, $O_2–As–O_3=106.0^\circ$
- $C_3–As–O_4=115.0^\circ$, $O_3–As–O_4=108.5^\circ$

Average $109.5^\circ\pm 4.5^\circ$

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