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The Crystal Structure of *p*-Iodobenzoic Acid Investigated by X-Ray Powder Diffraction

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Synopsis. The crystal of the title compound is monoclinic with space group $P2_1/a$, $a=30.36(3)$, $b=6.04(1)$, $c=4.16(1)$ Å, $\beta=97.4(1)°$ and $Z=4$. The crystal structure was solved from X-ray powder diffractometer data by the packing analysis based on an ellipsoid-model and by the pattern-fitting structure refinement. The final R (profile) value was 0.168. This structure is isostructural with that of *p*-bromobenzoic acid.

In order to obtain single crystals of *p*-iodobenzoic acid suitable for X-ray intensity data collection, many attempts were made but they were all unsuccessful. Then the crystal structure was solved from X-ray powder diffractometer data using the method of pattern-fitting refinement with structural constraints.[1)]

Experimental

Crystals grown from an aqueous solution occur as very thin lamellas with the well-developed (100) plane. The intensity measurements were made on an X-ray powder diffractometer (Rigaku-Denki, Ru-200PL) with Cu $K\alpha$ radiation monochromatized by a curved graphite monochromator. A scan was made from 11 to 44° in 2θ with scanning speed of 0.25 °/min; in this angular range there are 82 contributing reflections. The background-corrected intensities were measured on the chart in steps of 0.05° (in 2θ) over the above angular range. The intensity measurements of the profile with 2θ greater than 44° were not made because a large number of diffraction peaks overlap each other considerably.

Crystal data of this compound have been reported by Toussaint.[2)] They are: monoclinic with cell dimensions, $a=30.46$, $b=6.05$, $c=4.16$ Å, $\beta=97°19'$, space group $P2_1/a$ and $Z=4$. The cell dimensions were refined by using diffraction data from a powder sample mixed with the silicon powder as internal standard. They are $a=30.36(3)$, $b=6.04(1)$, $c=4.16(1)$ Å and $\beta=97.4(1)°$.

Structure Determination

Trial structures were obtained by the packing analysis based on an ellipsoid-model[3)] which was obtained on the assumption that two planar molecules with conventional bond lengths and angles form a centrosymmetric dimer and the three orthogonal molecular axes coincide with the principal axes of the ellipsoid. The dimensions of the ellipsoid, 10.6, 3.0, and 1.8 Å, were obtained from a consideration of van der Waals radii of the atoms. The center of the ellipsoid was placed on the center of symmetry and its orientation was described by the use of Eulerian angles ϕ, θ, and ψ, where ϕ and θ are the ordinary polar-coordinate angles of the major axis L of the ellipsoid referred to the axes a and b* and ψ is the angle measuring the rotation about the axis L.

By the above method five sets of ellipsoid-packing each having quite different packing mode were obtained. After transforming the coordinates of atoms in a molecule referred to the principal axes of the ellipsoid to those referred to the crystal axes, we calculated powder intensity profiles by using the expression given below. In the structure-factor calculation, an overall temperature factor, $B=3.0$ Å^2, was used and the contribution from the H atoms was neglected. A structure having an intensity profile strikingly similar to the observed one was chosen as the starting structure for refinement; the Eulerian angles were $\phi=165$, $\theta=55$, and $\psi=150°$. The R value defined by

$$R = \sum_i |y_i(\text{obsd}) - y_i(\text{calcd})| / \sum_i y_i(\text{obsd})$$

was 0.26, where y_i is an intensity at a given point $2\theta_i$ in a profile and is expressed in the form

$$y_i = \sum_k \left[\frac{2}{3} I_k \Omega(2\theta_i, 2\theta_{k1}) + \frac{1}{3} I_k \Omega(2\theta_i, 2\theta_{k2}) \right].$$

Here summation is taken over all possible contributing reflections at $2\theta = 2\theta_i$; I_k is the calculated intensity of reflection k for Cu $K\alpha$; $\Omega(2\theta_i, 2\theta_{k1})$ and $\Omega(2\theta_i, 2\theta_{k2})$ are the line shape functions for Cu $K\alpha_1$ and Cu $K\alpha_2$ respectively and are represented by Cauchy functions with full width (in 2θ) at half height of a peak, H_k, given by

$$H_k = v \tan\theta_k + w,$$

where v and w are parameters.

The pattern-fitting refinement was made by visual comparison of observed and calculated intensity profiles. The parameters varied in the refinement were: three Eulerian angles, one C–I bond distance, one temperature factor for the I atom and two for the peak shape. Note that the refinements of positional and thermal parameters for the atoms except the I atom were not made since their contributions to the structure factors can be considered to be very small as compared with that of the I atom. The final values of the parameters are: Eulerian angles, $\phi=166$, $\theta=56$, and $\psi=150°$, C–I$=2.03$ Å (initial value, 2.15 Å), $B=3.0$ Å^2 and peak shape parameters, $v=0.24$ and $w=0.13$. The final R value is 0.168 for

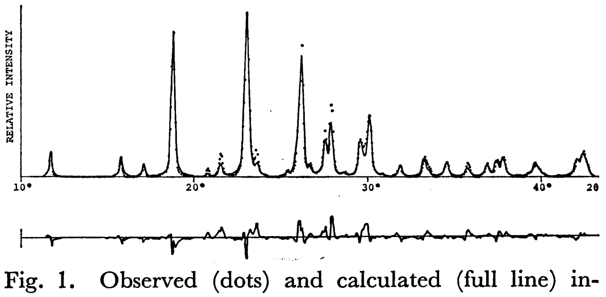

Fig. 1. Observed (dots) and calculated (full line) intensity profiles for *p*-iodobenzoic acid. The lower trace is the difference between observed and calculated profiles.

Table 1. The final fractional coordinates for non-hydrogen atoms

Atom	x	y	z
C_1	−0.0874	0.3156	0.1660
C_2	−0.0800	0.5223	0.3068
C_3	−0.1156	0.6508	0.3744
C_4	−0.1585	0.5726	0.3011
C_5	−0.1659	0.3660	0.1603
C_6	−0.1303	0.2375	0.0928
C_7	−0.0493	0.1779	0.0936
O_1	−0.0577	−0.0010	−0.0283
O_2	−0.0121	0.2459	0.1572
I	−0.2106	0.7609	0.3996

The bond lengths are C–C(benzene ring) = 1.39 Å, C_1–C_7 = 1.49 Å, C–O = 1.20 Å, C–I = 2.03 Å, and OH···O = 2.65 Å.

631 intensities from 11.5 to 43° in 2θ.

Figure 1 shows observed and calculated intensity profiles together with the differences between them. The final coordinates of non-hydrogen atoms are listed in Table 1. The structure viewed along the c axis is shown in Fig. 2. This structure is isostructural with that of *p*-bromobenzoic acid.[4)]

In conclusion we may say that the use of structural constraints in the powder-pattern-fitting refinement[1,5)] is certainly very useful, especially when only low-angle intensity data with highly overlapped peaks are available. Further, in such a case, it would be very important to find a starting structure very close to the final one for obtaining a stable refinement.

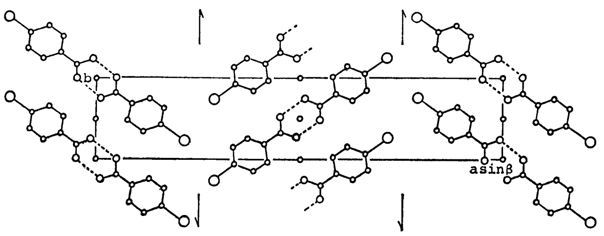

Fig. 2. The crystal structure viewed along the c axis.

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