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THE CRYSTAL STRUCTURE OF p-HYDROXYBENZALDEHYDE

Fujiko IWASAKI, Masahiro SATO, and Ariyuki AIHARA
Department of Materials Science, The University of Electro-Communications, Chofu-shi, Tokyo, 182

The crystal structure of p-hydroxybenzaldehyde was determined by a three-dimensional X-ray analysis. The molecules are linked by the O-H···O=C intermolecular hydrogen bond between hydroxyl and aldehydic groups parallel to the a axis, forming a zig-zag chain elongated along the b axis. The distance of the hydrogen bond, O···O, is 2.67 Å.

In order to establish the hydrogen-bonded system of the title compound, the crystal structure analysis was undertaken.

Commercially available p-hydroxybenzaldehyde was recrystallized from chloroform to give colorless flat plates. The crystal data are: $C_7H_6O_2$, M.W.= 122.12; monoclinic, a=6.453 (5), b=13.810 (8), c=7.044 (6) Å, β=107.94 (9)°, V=597.2 Å^3; Z=4, D_x=1.358, D_m=1.35 g.cm^{-3}; space group $P2_1/c$.
The intensity data were collected from integrated equi-inclination Weissenberg photographs around the a and b axes, 0kℓ~4kℓ and hOℓ~h9ℓ, using CuKα radiation. The intensities were measured with a microphotodensitometer. A total of 762 non-zero reflections was observed.

The structure was solved by a symbolic addition method[1] using the program DP-system written by R. S. Hall. All hydrogen atoms were located from a difference Fourier map. Block-diagonal least-squares refinement with anisotropic temperature factors for the carbon and oxygen atoms and with isotropic temperature factors for the hydrogen atoms was carried out and the R value was reduced to 0.084 for all observed reflections except six strong ones.

Bond lengths and angles are shown in Fig. 1. Standard deviations in the bond distances and angles for the carbon and oxygen atoms are 0.007 Å and 0.45°, respectively. The average C-C distance in the benzene ring is 1.386 Å, but the C(3)-C(4) distance (1.376 Å) is slightly shorter than the rest of benzene ring distances. The molecule is approximately planar, deviations from the mean plane being within 0.015 Å.

Fig. 2 shows the molecular arrangement viewed along the c axis. The molecules are linked by the O-H···O=C intermolecular hydrogen bond between the hydroxyl and aldehydic groups parallel to the a axis, forming a zig-zag chain elongated along the b axis. The distance of the hydrogen bond, O···O, is 2.67 Å.

Aihara and Shirota have suggested from their infrared measurement that the hydrogen bond in this crystal is very likely of the type, O-H···O-H···O-H

and that the carbonyl group is not involved in the hydrogen bond formation[2]. The present result, however, dose not support their suggestions.

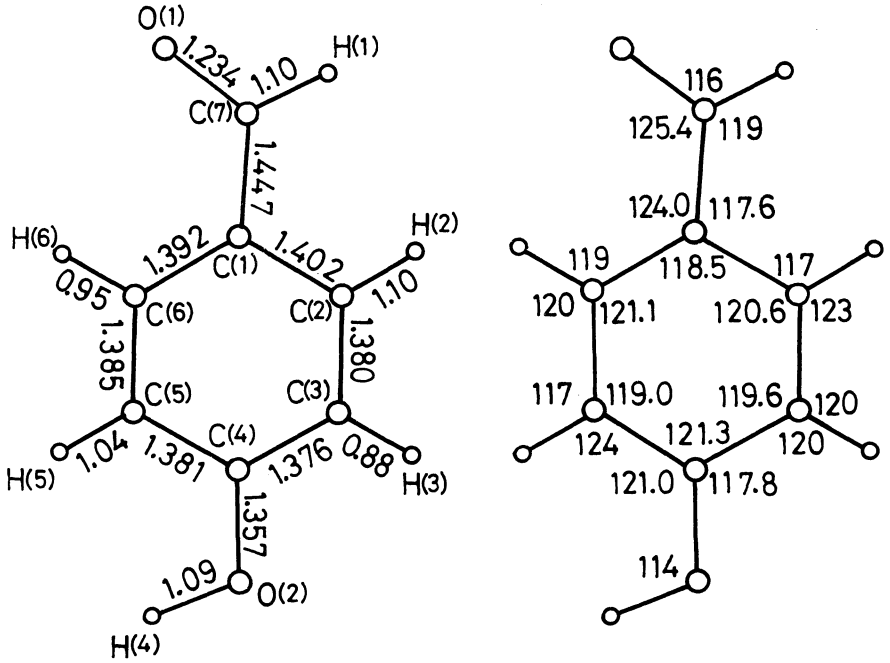

Fig. 1 Bond distances and angles

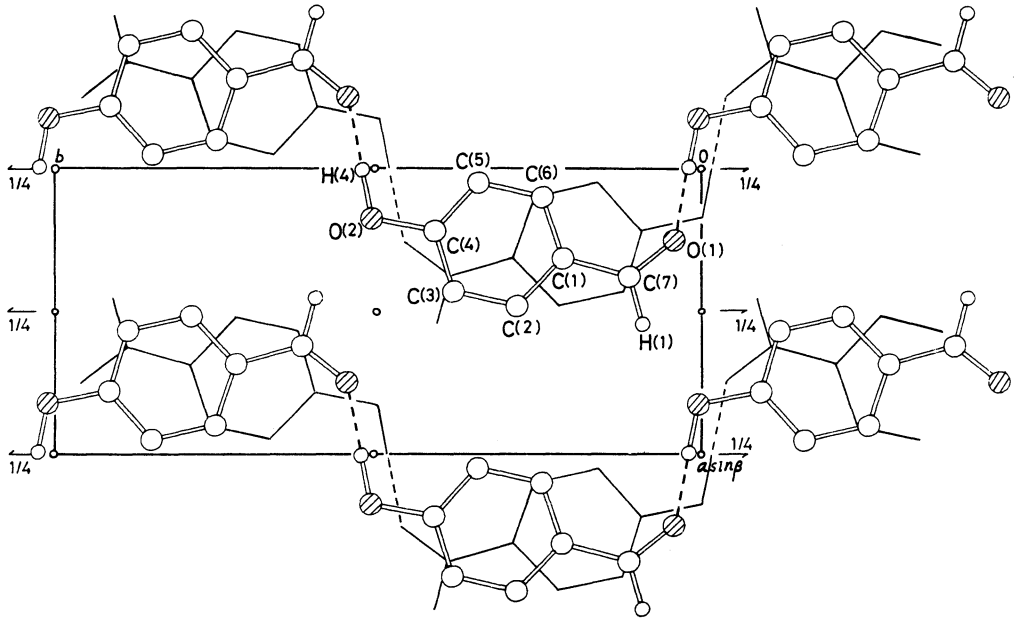

Fig. 2 The crystal structure viewed along the c axis

References

1) I. L. Karle and J. Karle, Acta Crystallogr., 16, 969 (1963).
2) A. Aihara and Y. Shirota, Bull. Chem. Soc. Japan, 45, 935 (1972).

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