The Crystal Structure of Pyromellitic Acid Dihydrate (Benzene-1,2,4,5-tetracarboxylic Acid Dihydrate)

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Since the pyromellitic acid dihydrate, $C_6H_2(COOH)_4 \cdot 2H_2O$ has four –COOH and two H_2O, it is of interest to elucidate the steric hindrance of adjacent carboxyl groups and the hydrogen bond formation in this crystal and to compare the structure of this compound with those of other similar carboxylic acids.

The crystal of this compound is triclinic, with cell dimensions of $a=10.05$, $b=6.46$, $c=5.44$ Å, $\alpha=74.5°$, $\beta=112.2°$, and $\gamma=77.3°$. The space group is $P\bar{1}$, and the unit cell contains one molecule. The calculated density is 1.64 g/cm³, while the observed value obtained by the flotation method is 1.63 g/cm³. The intensities were estimated visually from Weissenberg photographs around b and c axes taken with Cu$K\alpha$ radiation; 1070 were recorded, but of these 148 were too weak to be measured.

The crystal structure was derived by a consideration of Patterson maps and was confirmed by three-dimensional Fourier syntheses. The positional and thermal parameters of each atom thus obtained were refined by the block-diagonal least-squares method. The R factor is 0.09 at the present stage.

The projection of the crystal structure along the c axis and the molecular configuration of the pyromellitic acid are shown in Figs. 1 and 2 respectively. The average C(ring)–C(ring) distance is 1.39 Å, and the average C(ring)–C(carboxyl) distance is 1.49 Å. One carboxyl group is twisted by 21.4°, and the other is twisted by 74.5°, out of the plane of the benzene ring. The C–O(H) and C=O distance differ significantly from each other, the average values being 1.31 and 1.21 Å respectively. Four types of hydrogen bonds, with the average O–H···O distance of 2.72 Å, form a three-dimensional network, as shown in Fig. 1. Each molecule is joined to two other molecules through hydrogen bonds around the center of symmetry, forming an endless chain in the [1 $\bar{1}$ 1] direction. Water molecules are arranged on the plane parallel to [1 1 0], which hold the chains together by means of hydrogen bonds. A detailed account of this work will be presented in the near future.

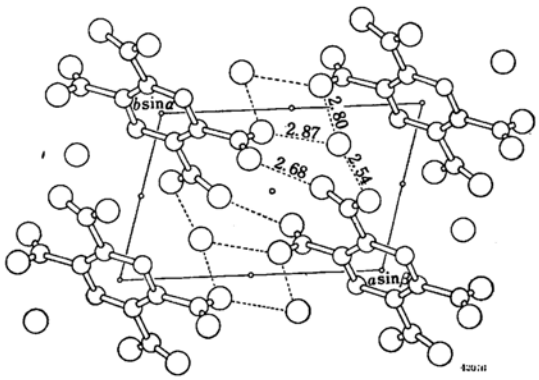

Fig. 1. The projection of the crystal structure along the c axis.

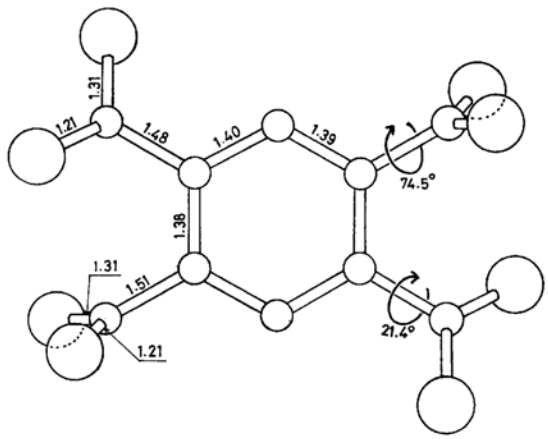

Fig. 2. The projection of the pyromellitic acid on a benzene ring.