

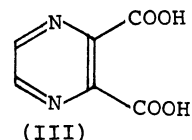
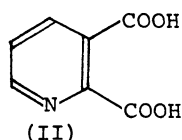
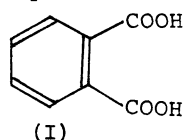
THE CRYSTAL STRUCTURE OF PYRAZINE-2,3-DICARBOXYLIC ACID DIHYDRATE

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The crystal structure of pyrazine-2,3-dicarboxylic acid dihydrate has been determined by X-ray diffraction method. The lone pairs of N atoms in the pyrazine ring participate in H-bonds, while some lone pairs of O atoms are free from H-bonds. This fact suggests that the O-H...N bond is energetically more favored than the O-H...O bond in carboxylic acids with an aromatic six-membered ring.

This work is a part of a series of studies on the O-H...N bonding in solids. Pyrazine-2,3-dicarboxylic acid(III) has the same framework and isoelectronic structure as phthalic acid(I)<sup>1)</sup> and quinolinic acid(II)<sup>2)</sup>. The molecular conformations



and H-bonding schemes of (I) and (II) are quite different from each other in solids. These differences are caused by the existence of a N atom in (II), which can act as an acceptor of the H-bond. Therefore, the crystal structure analysis of pyrazine-2,3-dicarboxylic acid(III) dihydrate was undertaken to elucidate the effect of N atoms in the aromatic six-membered ring on H-bond formation in solids.

Crystals were obtained by recrystallization from aqueous solution. The crystal data are:  $C_6H_4N_2O_4 \cdot 2H_2O$ , M.W. = 204.14; monoclinic,  $a = 5.394(4)$ ,  $b = 13.159(5)$ ,  $c = 11.934(7)$  Å,  $\beta = 98.1(1)^\circ$ ,  $V = 838.6$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.617$ ,  $D_m = 1.60$  g/cm<sup>3</sup>, space group C2/c. Intensity data were collected by means of the equi-inclination integrating Weissenberg technique using CuK $\alpha$  radiation. The independent 866 reflections were observed and no corrections were made for absorption and extinction.

The structure was easily solved by inspecting the sharpened Patterson map. All H atoms were found from a difference Fourier map. Block-diagonal least-squares refinements with anisotropic temperature factors for non-hydrogen atoms and isotropic temperature factors for H atoms were carried out and the conventional R value was reduced to 6.10% for all observed reflections. The coordinates are listed in Table 1.

Bond lengths and angles are given in Fig. 1. Standard deviations are: C-C, C-N and C-O = 0.003 Å, C-H and O-H = 0.02 ~ 0.04 Å, C-C-C, C-C-N, C-C-O and C-N-C = 0.2°, N-C-H and C-O-H = 2 ~ 4°. There is no intramolecular H-bond, contrary to that found in (II), between the adjacent carboxyl groups. The carboxyl groups twist by 33.7° out of the plane of the pyrazine ring, reducing the repulsion between the O atoms. The differences between the C(2)-C(2') and C(3)-C(3') and between the N(1)-C(2) and N(1)-C(3) bond lengths, 0.019 and 0.012 Å, respectively, are significant judging from

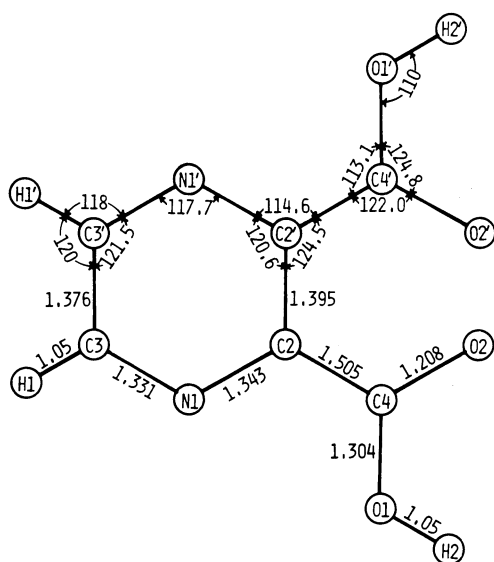


Fig. 1. Bond lengths and angles.

Interestingly, the present crystal structure resembles that of (I), even though the present crystal has waters of crystallization and intermolecular H-bonds are formed through the water molecules. Clearly, the water molecules play a role of forming O-H...N bonds in which the lone pairs of N atoms in the pyrazine ring can act as acceptors. This fact suggests that the lone pairs of N atoms in the aromatic ring have a stronger ability for H-bond formation than those of O atoms in water or the carboxyl group.

their estimated standard deviations. Similar differences are found in (II). The C(2)-N(1)-C(3) bond angle is 117.7; this value indicates that protonation on the N atom does not occur in this crystal.

Figure 2 shows the molecular arrangement viewed along the a axis. The acid molecules lie on the two-fold axes like (I) and are joined through the H-bonds (O-H...O; 2.563, 2.923 Å, O-H...N; 2.841 Å) to six neighboring water molecules, forming the three-dimensional network. From our study of pyridine-carboxylic acids<sup>3)</sup> and this crystal structure, the relationship between the O-H...N and  $\overset{+}{N}$ -H... $\overset{-}{O}$  bonds may be as follows. When the donor group for the N atom is able to take the resonance scheme, like the carboxyl group, the  $\overset{+}{N}$ -H... $\overset{-}{O}$  bond is formed, and when the donor group is not so, like the water, the O-H...N bond is formed in solids. Interest-

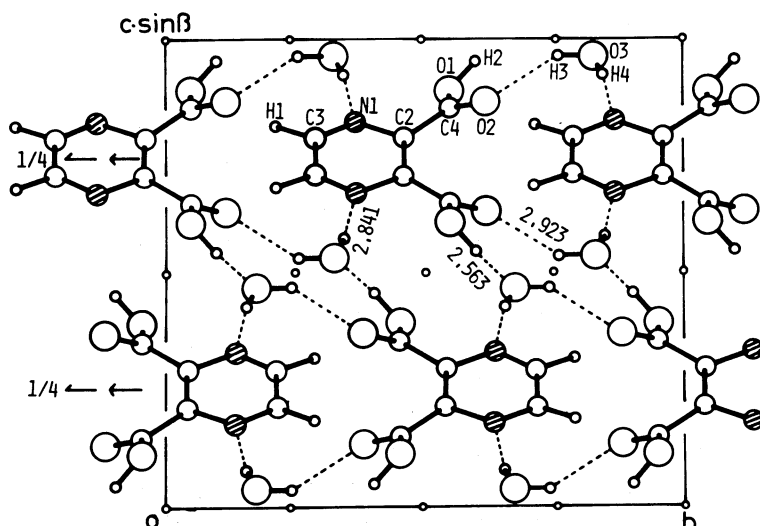


Fig. 2. The crystal structure viewed along the a axis.

Table 1. Atomic coordinates.

Atom	x	y	z
N(1)	0.3290	0.3701	0.8262
C(2)	0.4202	0.4577	0.7912
C(3)	0.4116	0.2939	0.7863
C(4)	0.3544	0.5506	0.8544
O(1)	0.1349	0.5446	0.8878
O(2)	0.4978	0.6210	0.8740
O(3)	0.4476	0.8266	0.9607
H(1)	0.344	0.215	0.814
H(2)	0.119	0.600	0.950
H(3)	0.458	0.761	0.962
H(4)	0.545	0.846	0.929

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- \*) He succumbed to disease at 5 August, 1973.

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